

October, 1935

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME VIII

NUMBER 4

MICRONEX BEADS

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2. It must be "compact and dense" to save freight charges.
3. It must retain its form during shipment to all parts of the world.
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5. It must handle and flow easily to facilitate weighing out and handling to and into the mills.
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RUBBER CHEMISTRY AND TECHNOLOGY

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Vol. VIII

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CONTENTS

General Subjects

	PAGE
Rubber Division Activities.....	xxxv
New Books and Other Publications.....	xxxvi

Reprinted Papers

The Physico-Chemical Properties of Latex and Their Significance in Manufacture. By E. W. MADGE.....	501
Heat Changes in the Vulcanization of Rubber. I. Qualitative Tests on a Comparative Basis. By HUKIO HORIE and KIKUO MORIKAWA.....	514
The Raman Spectrum of Rubber. By S. D. GEHMAN.....	521
Elastic Hysteresis and Increase in Tensile Strength at Low Temperatures. By S. KHVOSTOVSKAYA and B. MARGARITOV.....	522
The Shock-Absorbing Quality of Rubber. By L. FRUMKIN and V. MARGARITOV.....	528
The Determination of the Optimum Vulcanization by Means of the Residual Elongation. By A. KUSOV.....	548
Semi-Ebonite. By P. A. GIBBONS.....	554
Fatty Acid Softeners in Rubber Compounding. By C. M. BLOW and T. L. GARNER.....	571
Theory and Application of the Parallel-Plate Plastimeter. By J. R. SCOTT..	587

Entered as second-class matter May 12, 1928, at the Post Office at Easton, Pennsylvania, under the Act of August 24, 1912.

The Problem of the Evaluation of Reclaimed Rubber by Analytical Methods. By F. KIRCHHOF.....	597
Studies on the Acetone Extraction of Raw Rubber. By HIDEMARO ENDO	604
Research on Modified Rubbers. Part V. Technological Properties of Chlorinated Rubbers from Latex. Part Va. Technological Properties of Rubber Oxidation Products. By P. SCHIDROWITZ.....	613
Research on Modified Rubbers. Part VII. Expanded Chlorinated Rubber. By P. SCHIDROWITZ and C. A. REDFARN.....	616
Appendix. The Composition of Some Chlorinated Rubbers. By G. F. BLOOMFIELD, E. H. FARMER and C. H. MILLER.....	622
Rubberone. By H. P. STEVENS and W. H. STEVENS.....	624
Rubber in Paints. By H. P. STEVENS, W. H. STEVENS, and NOEL HEATON.	627
Rubber in Lubricants. By H. P. STEVENS, W. H. STEVENS, and M. B. DONALD.....	629
Preparation from Rubber of Plastic Materials Suitable for the Manufacture of Films and Threads. By H. I. WATERMAN, C. G. H. MAX, and J. J. LEENDERSTE.....	632
Properties of Latex-Insulated Wire. By J. McGAVACK.....	635
Koroseal, A New Plastic. By S. L. BROUS and W. L. SEMON.....	641

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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New Books and Other Publications

Rubber—Physical and Chemical Properties. By T. R. Dawson and B. D. Porritt. A Technical Handbook published with the co-operation of The Rubber Growers' Association, Inc., and The Research Association of British Rubber Manufacturers. Published by The Research Association of British Rubber Manufacturers, Croydon, England. Price 45s., post free.

For a long time the need has been felt for reliable books of reference summarizing scientific and technological data relating to rubber and its various compounded forms.

The publication now under reference deals more especially with technical data obtained in evaluating and measuring the various properties of rubber and rubber compounds. The dividing line between fundamental and applied scientific knowledge is often very indistinct and arbitrary, and the present volume avoids the fundamental side, except in so far as is necessary by way of general explanations in the various chapters.

The main text occupies 545 pages (demi-quarto), consisting for the most part of tabulated data dealing with the chemical and physical properties of latex, coagulum, raw rubber, soft vulcanized rubber, sponge and cellular rubber, and hard rubber (ebonite).

The breakdown of the chemical and physical properties varies naturally with the group concerned, but an idea of its range and completeness may be gained from that concerned with soft vulcanized rubber, which is treated chemically as to: changes due to natural aging; changes due to heat and heat-aging; changes due to action of light; oxidation in oxygen; comparisons of changes due to various aging conditions; attack by chemical reagents; reclaiming and desulfurization; odor; toxicity; and physically as to: tensile stress-strain properties; permanent set; volume change due to extension; energy relations; tensile fatigue; anisotropy (grain); hardness; compression; abrasion; tear-resistance; coefficient of friction; thermal properties; thermo-elastic properties (Joule effect); optical properties; electrical properties; swelling in organic liquids and vapors; water absorption; behavior towards gases; behavior as a solvent of solid substances; specific gravity; porosity; acoustic properties.

That it is impossible to pass its subject matter in critical review will be evident. It has been compiled from 1400 publications, entailing the consultation of some 300,000 references.

All that we can do at the present stage is to mention its general features, and congratulate its authors and their associates on having achieved so creditably something so useful and so much worth while.

In an excellent foreword, Sir Herbert Wright surveys the wide field of interest which the publication will help to satisfy. He mentions that lengthy sections are devoted to the various treatments of latex, and to the effect of estate-factory materials and methods on the ultimate properties of rubber. Thus it should appeal to the rubber research worker, be the chemist, physicist, or engineer, since by the production of this survey of quantitative information, it is possible to see for the first time how many rubber problems are clamouring for investigation. Rubber manufacturers will find the work of great value, since the detailed results of the effects of large numbers of compounding ingredients clarify complex subjects in the simplest way. Finally, it will appeal to the consumer of rubber goods, particularly to those in the construction professions, from the standpoint of the infiltration of rubber into new industrial applications.

The form and arrangement of the tabulated matter follows in many respects the

excellent model established by G. S. Whitby in the International Critical Tables. There is a selected bibliography of rubber literature, and the bibliography of authors cited is probably the most complete that has ever been compiled. It is a publication for which, even in this ever-changing industry, there will be a constant demand for reference. [From the *Bulletin of the Rubber Growers' Association*.]

Meccanica Del Pneumatico. A Reprint. By R. Ariano. Published by Direzione-Amministrazione, Via Petrella, 14, Milan, Italy. 30 pp.

Written in Italian, this article reprinted from *L'Industria* fully covers the mechanics of pneumatic tires. It is illustrated with several technical charts and graphs, and contains many technical equations. A portion of the article is devoted to a discussion of fabric stresses in pneumatic tires, while mention is made of the importance of good roads on tire performance. [From *The Rubber Age* of New York.]

Rubber Producing Companies—1935. Compiled by the Mincing Lane Tea & Rubber Share Brokers Association, Ltd., 14 Mincing Lane, London, E. C. 3, England. Published by The Financial Times, Ltd., 72 Coleman St., London, E. C. 2. Boards, 578 pages, 5 by 8 inches. Indexed.

This standard work is the largest and most complete volume of reference on the subject of rubber planting companies, and is intended to help those interested in this field of investment. The authentic and exhaustive information concerning over 575 companies includes capital, acreage, latest accounts, crops, purchase price, dividends, forward sales, estimates, etc. Particulars are also given of many companies with tea and coffee interests, also a list of directors and secretaries of rubber companies. [From the *India-Rubber World*.]

Proceedings and Papers of the Fifth Conference of the Technical Experts in the Printing Industry and Organization Meeting of Graphic Arts Research Bureau Held in Philadelphia, Pa., October 8-9, 1934. American Society of Mechanical Engineers, 29 W. 39th St., New York, N. Y.

Among the papers reported are "Rubber Plates for Letter-Press Printing," by Ralph H. Schwarz and J. Homer Winkler, and "Observations on the Technology of Rubber Plate Manufacture," by W. J. Roscoe, with discussions by H. W. Haydock, Hylton Swan, E. M. Frankel, Henry Kohlus, J. G. E. Wright, and W. M. Lee. [From the *India-Rubber World*.]

The Contribution of the Chemist to the Rubber Industry for the Advancement of Civilization. A Reprint. By Harry L. Fisher. Issued by the U. S. Rubber Company, 1790 Broadway, New York City.

Seeking to draw a definite line between an ordinary experimenter and a chemist, Dr. Fisher, associated with the General Laboratories of U. S. Rubber, raises a pertinent question, *i. e.*, was Charles Goodyear a chemist? He suggests, in this readable article, that we include in the definition of a chemist "one who uses chemicals to such good advantage as to produce new and useful goods." The balance of this article is devoted to a brief review of the more important contributions of chemistry to the rubber industry within recent years including the discovery of accelerators of vulcanization and of antioxidants. [From *The Rubber Age* of New York.]

The Story of the Elastotype. B. F. Goodrich Co., Akron, O.

This booklet is printed from molded rubber plates. It answers questions about rubber, tells when and where to use it, and states its advantages and disadvantages. Various kinds of paper are used in the booklet to demonstrate the facility and

perfection with which printing can be done by molded rubber plates with colored and other inks. [From the *India-Rubber World*.]

Modern Shoe Dressings. The Raw Materials, Manufacture, and Applications. By W. D. John. With a Chapter on Shoe Cleaners and Special Cleaning Reagents. R. H. Johns, Ltd., Newport, Mon., England. 1934. (The Chemical Publishing Co., 175 Fifth Ave., New York, N. Y.) Cloth, 153 pages, 6 by 10 inches. Index. Price \$5.

This handbook of materials, data, and formulas designed for leather finishing contains much of interest and value for rubber chemists and technologists concerned with finishes for rubber footwear, artificial leather, druggists' sundries, etc. [From the *India-Rubber World*.]

Petroleum—The Story of an American Industry. Prepared and published by the American Petroleum Institute, 50 West 50th Street, New York City. 95 pp. 15 cents.

Representing the second edition of the booklet "Oil," published by the American Petroleum Institute in 1930, this latest edition is larger and answers many questions which have arisen since publication of the original booklet. The purpose of "Petroleum" is to tell, in simple terms, of the operations and services involved in the transformation of this natural resource into useful products, a purpose it successfully accomplishes. A detailed description of the industry's numerous operations, services, and products would, of course, require a mammoth volume. Of particular interest to the rubber industry is the chapter on "Uses of Petroleum Products" which includes brief descriptions of distillates and residues. [From *The Rubber Age* of New York.]

1935 Chemical Guide Book. (Eleventh Edition.) Published by Chemical Markets, Inc., 25 Spruce Street, New York City.

Divided into four sections the 11th annual chemical guide includes a combined catalog of chemical firms, a buying guide and directory for chemicals and allied products, a geographical directory of chemical and allied industries, and lists of prices and trade associations. 108 pages have been added to this new edition due to the listing of 153 additional chemicals and 160 new synonyms. Approximately 3500 firms are listed as being members of the chemical and allied industries. The section devoted to prices depicts high and low prices for some 1500 chemicals for the years 1933 and 1934. [From *The Rubber Age* of New York.]

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 10, No. 5,
pages 393-410, February, 1935.]

The Physico-Chemical Properties of Latex and Their Significance in Manufacture

E. W. Madge

The first physico-chemical property of latex to be discussed is that of viscosity, if latex can be said to have a viscosity. As will be seen later, this property is so important in many manufacturing processes, such as extrusion, dipping, and centrifuging that the fundamentals must be understood.

Latex, as is well known, is a suspension of irregularly shaped particles, many pear-shaped, in an aqueous medium which itself contains an appreciable proportion of other dissolved and suspended matter. These particles, according to present ideas, are surrounded by a strong adsorption layer, which influences very considerably the properties of the latex. As a result of its composite structure, latex and more particularly latex compounds have rather interesting properties.

From the point of view that latex creams under gravity, that the particle carries an appreciable electric charge, and depends partly on this for its stability, and that the swelling of the actual particle in water is very small, it may be called hydrophobic. On the other hand, in view of its behavior with respect to dehydrating agents, the manner in which it forms aqueous voluminous gels, and more particularly in its reaction to shearing forces, latex may be classed as hydrophilic. Its hydrophilic character is conditioned by the material adsorbed on the surface of the particles and is more pronounced in compounded and treated latices.

When the question was raised as to whether latex had a viscosity, what was meant was this. Viscosity (η) is ordinarily defined for a normal liquid by the equation: $F = \frac{\eta \cdot dv}{dy}$, that is, the viscosity coefficient is the tangential force per unit area

per unit velocity gradient or, in other words, for a normal liquid the shearing force is directly proportional to the velocity gradient. With latex, as with many other colloids, the shearing force is not a linear function of the velocity gradient, but varies in a more complex fashion, particularly for low rates of shear.

As indicated previously the phenomenon is not confined to latex, but is exhibited by many other colloids and suspensions, the anomalous viscosity associated with low rates of shear being termed "the structural viscosity."

This may be noticed, for example, in dipping, particularly with some thickened mixings where the rate of withdrawal is slow. The withdrawal times, apart from drainage effects, affect the effective viscosity and the weight of the deposit.

Through the kindness of the Birmingham Central Technical College it was possible to use a rotating cylinder viscometer for the examination of the viscosity of latices. The results obtained with the instrument show the effect indicated diagrammatically in Fig. 1.

In Fig. 2 may be seen curves showing that the viscosity of Dunlop 60 per cent latex varies with the alteration in angular velocity of the rotating cylinder.

Hence, latex and many other colloids do not behave like normal liquids in their flow properties, but like pseudo-plastics. That is, they have pseudo-yield values which may be arbitrarily defined by tracing back the straighter portion of the curve

shown in Fig. 1 until it cuts the abscissa axis. There is actually no sharp yield point.

This is of importance when the measurement of the viscosity of latex is considered both for routine and other purposes, and it should be understood that latex includes treated latex and latex compounds.

A simple instrument for the checking and control of the viscosity of latex mixings has been used for a considerable time by the Dunlop Rubber Company, and is a modified form of Redwood Oil Viscometer (*Twiss, Trans. Inst. Rubber Ind.*, 6, 421 (1930)). The instrument is made from Staybrite steel, has interchangeable jets, and is easy to clean. The measurement is simply the time of flow through a suitable jet of 50 cc. of the mixing after filling to a fiducial mark. The jets are 1.5 mm. long, and of various diameters, for example, $\frac{1}{8}$ in., $\frac{3}{16}$ in., and $\frac{3}{32}$ in. This instrument, though very well suited to routine control work, cannot be used for the determination of absolute values for viscosity. Care must be taken in interpreting

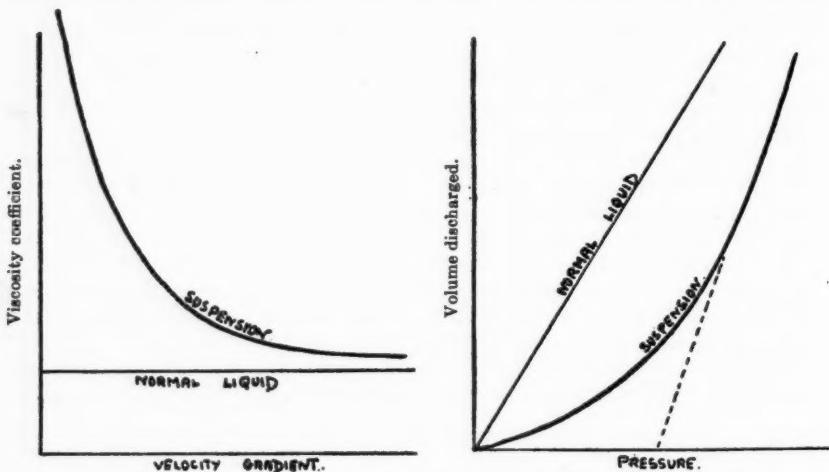


Figure 1

the readings for the following reasons. The readings are reliable if the time of flow is fairly short, that is, if the straighter part of the curve shown in Fig. 1 is considered. If, however, the mixing is very thick or thixotropic and the time of flow very long for a given jet, the region of variable viscosity is approached and the results are not so reliable. In general, it is not possible to extrapolate from one jet to another, and control tests for one mixing should be carried out with one jet. This is due to the kinetic energy correction and to the Couette correction for such short, large diameter jets. The latter expresses the deviation from the result expected were the jet of infinite length.

The instrument described by Sutton (*India-Rubber World*, 85, 56 (1932)), which consists of a longer capillary fed from a reservoir, has many of the disadvantages that have just been mentioned, and, in addition, lacks robustness and is more difficult to clean.

An alternative method that has been proposed and that is used for obtaining an interpretable figure is to use a capillary viscometer, but to make sure that one is working well out on the straight part of the curve of Fig. 1. Then following Bing-

ham, instead of using Newton's law, we may write: $F - f = \frac{\eta dv}{dy}$. This means that the force must reach a certain value f before flow takes place. The arbitrary interpretation of f is obtained, as we have seen, by producing the curve back to cut the axis. The fact that flow does take place at pressures lower than those corresponding to the yield value has been attributed by Bingham to seepage, which is presumably a segregation of the phases. Such an effect is observed in extrusion, for example, in thread manufacture when low pressure heads are used, the formation of cream, *i.e.*, segregation of the phases resulting in stoppages. To overcome this, very short jets not greater than 2 mm. in length were designed (see British Patent 367,104 (1931)).

The determination of the viscosity is carried out by taking two observations of the

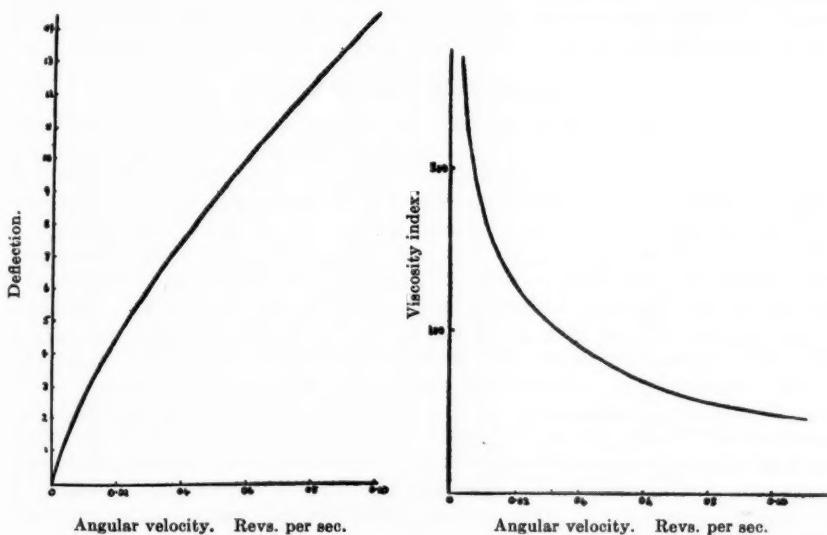


Figure 2—Effect of Rate of Shear on Viscosity of 60% Latex

flow for two pressure heads which lie on the straight portion of the curve; f is thereby eliminated. A determination of this nature gives a mean value for the viscosity of 60 per cent latex prepared by centrifuging of 0.4–0.5 per cent alkalinity, of 40–43 centipoises at 25° C. For an ordinary 38 per cent latex of 1 per cent ammonia content, the viscosity has a value of 5 to 6 centipoises. The figures quoted in the literature, for example, by de Vries (*Archief Rubbertcultuur*, 7, 436 (1923)) and Bary (*Revue gén. Caoutchouc*, 11, 3 (1934)) are of the same order.

The rotating cylinder viscometer gives a value nearer 38 centipoises for the viscosity at 21° C. of a 60 per cent latex of 0.5 per cent alkalinity produced by centrifuging. This is at a high rate of shear, and when the latex is behaving more or less like a normal liquid. The higher value of 42 centipoises is noted at lower rates of shear.

A comparison may now be made of the actual viscosity figures for latex and for rubber solutions.

	Concentration	t° C.	Abs. Viscosity (C. G. S.)
Rubber solution	10 g. per 100 cc.	20.0	3.42
	20 g. per 100 cc.	21.7	77.3
	25 g. per 100 cc.	18.5	269.5
	27.5 g. per 100 cc.	21.2	447.7
	30 g. per 100 cc.	21.0	746.9
Latex	38 g. per 100 g.	20° C.	0.05 to 0.06
Latex (centrifuged)	60 g. per 100 g.	20°	0.4 to 0.43
Water	20° C.	0.01

The figures for rubber solutions in benzene are those of Abernethy (*India-Rubber J.*, 70, 775 (1925)). The differences are immediately apparent. Latex mixings of high rubber content are no more viscous than thin creams, whereas even very dilute rubber solutions have a thick consistency. The way in which latex so rapidly superseded rubber solutions in dipping processes is therefore not difficult to understand. A similar observation applies to all processes where it is desired to build up an appreciable thickness of rubber from latex as compared with solution.

Viscosity and Concentration

It may be enquired why 60 per cent is a popular concentration for the higher concentration latices prepared by processes other than those depending on evaporation, such as centrifuging, creaming, and filtration. The reasons are that such processes depend on the relative movement of the latex particles and the serum, *i. e.*, the separation of the rubber from the serum. In the case of centrifuging, the effective force is the centrifugal one, in creaming, gravity, and in filtration a pressure difference. According to the usual analysis, the resistance to motion of a particle for low velocities is directly proportional to the viscosity and the radius of the particle, and the force producing the motion is proportional to the cube of the radius of the particle and the difference between its density and that of the serum. Consequently, other things being equal, the lower the viscosity of the latex the better the separation. It so happens, therefore, that for practical rotor speeds in centrifuging, which are governed by other considerations than the merely mechanical, and for gravitational separation, the viscosity of a 60 per cent latex is approximately the upper limit. In other words, at this concentration the particles are beginning mutually to influence each other seriously and to enter into each other's sphere of action.

Consequently, methods which are able to reduce the viscosity, without affecting other factors having a bearing on the efficiency of centrifuging, are of importance.

The actual relationship between the viscosity of a latex and its concentration is shown in Fig. 3.

The values given on this curve were obtained with the Dunlop viscometer, using $\frac{1}{8}$ in. jet at 28° C., the ordinates being times of flow for 50 cc., the abscissae concentrations in grams per 100 grams of latex. As the viscosity effect is a volume effect, it would have been better to express the concentration in cc. per 100 cc. of latex. For the reasons mentioned previously, this curve cannot be taken as quantitatively accurate, as the rather sharp change in slope at a concentration of approximately 58 per cent differs for different jets. But the curve suffices to show the general characteristics of the relationship.

This curve was obtained by diluting a latex of 70 per cent concentration, which was prepared by an evaporation process using ammonia alone for stabilizing, the final alkalinity being 1 per cent. Dilution was carried out with 1 per cent ammonia solution. It is impossible to obtain a serum of exactly the same composition as that of a latex. Bary (*loc. cit.*) gives a similar curve having the same characteristics.

The question may now be asked, particularly as far as dipping processes are concerned, what should be aimed at—control of the viscosity or of the concentration? The viscosity is by far the more important, a very much bigger variation in deposit weight being obtained if the total solids are kept constant and the viscosity varied than if the viscosity is kept constant and the total solids altered. This is particularly the case for high concentration mixes, where the slope of the viscosity concentration curve is steep, and it needs only a small change in concentration to alter the viscosity enormously.

Figure 4 shows a curve for the weight of a deposit from a beach shoe type of mixing of concentration 66 per cent, whose viscosity was altered by small additions

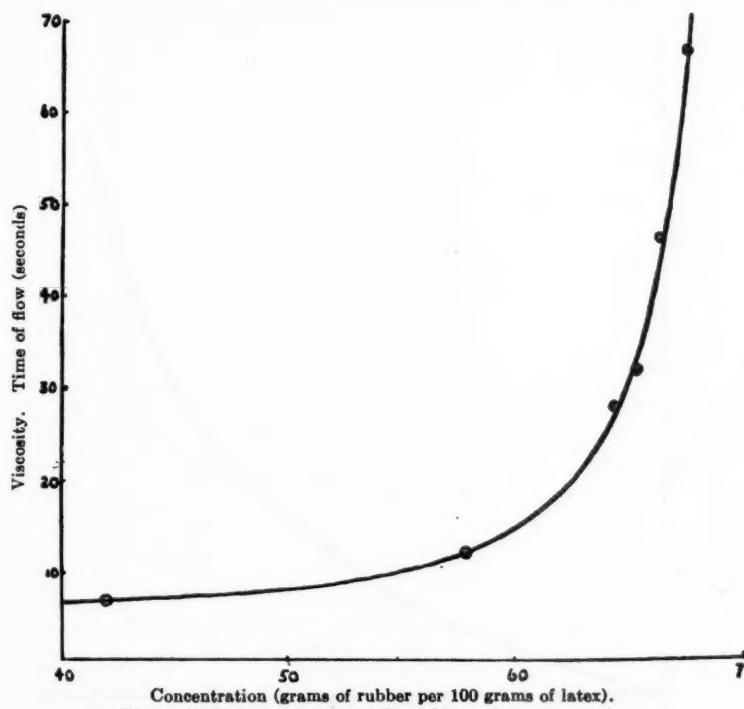


Figure 3—Relation between Viscosity and Concentration

of 0.3 per cent ammonia solution with little change in the concentration. The deposition was a non-ionic one, a beach shoe last being dipped into the mixing and slowly withdrawn in a standard time of 15 seconds, the deposit being set in 5 per cent acetic acid and subsequently dried. (The weights given are the weights of two superimposed dips.)

For low viscosity mixings, such as unthickened mixings of concentration below 60 per cent, the viscosity does not change very rapidly, and the weight of a non-ionic deposit depends to a greater extent on the total solids of the mixing. Thickening of a low concentration latex by means other than increasing concentration also increases the weight of a deposit considerably, but this then suffers from the disadvantage of increased drying shrinkage.

The same observations are also true for ionic dipping where internal coagulants

are used. As, however, viscosity changes are also in many cases indicative of stability changes, these will also affect to some extent the deposition weights when ionic dipping is used.

It may, therefore, be seen that for a manufacturing process, such as dipping, one of the most important routine controls for uniformity in the product is that of control of viscosity.

Viscosity and Temperature

In common with other colloidal suspensions, the viscosity of latex mixings

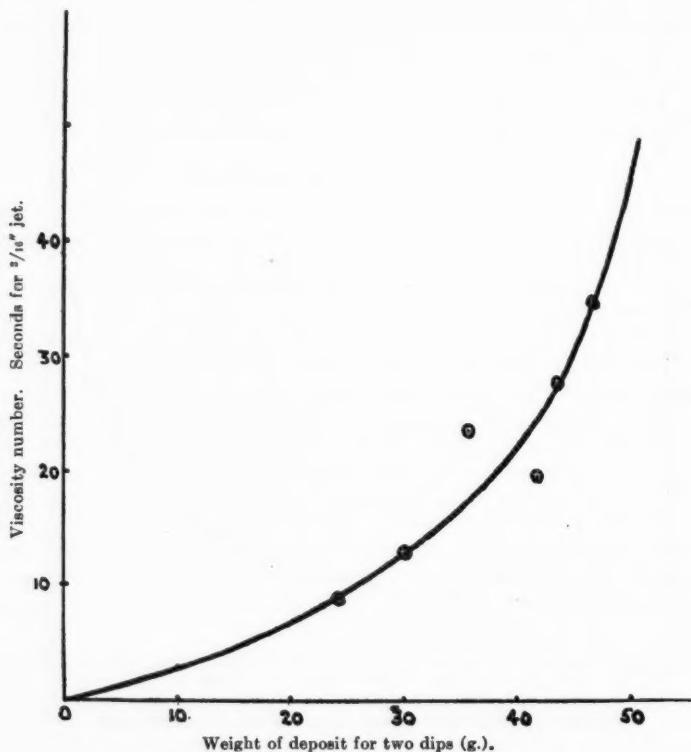


Figure 4—Effect of Viscosity on the Weight of Deposit

decreases rapidly with rise in temperature. The relation is probably a logarithmic one, of the form discussed by Andrade for liquids, $\log \eta = a + \frac{b}{T}$. The decrease of viscosity with temperature has not been used to any great extent, though a recent patent (British Patent 412,752 (1933)) claims that an increased separating efficiency in the centrifuging process may be obtained by heating the latex, due to the reduction in viscosity thereby obtained.

The Effect of Added Agents on Viscosity

In order to understand clearly the powerful effect of various agents on the viscos-

ity of latex and latex mixings, reference must be made to the composition of latex. The latex system consists of particles suspended in an aqueous medium. These particles are prevented from coalescing (1) by their charge, and (2) by the adsorption envelopes on their surfaces. Both these factors govern the mutual approach of the particles, which in turn governs the viscosity of the mixing. The methods by which the viscosity of a mix may be altered by agents fall therefore into three groups, by (1) influencing the charge on the particle, (2) altering the magnitude of the protective envelope, and (3) altering the viscosity of the aqueous serum itself. The three groups must necessarily be somewhat interconnected, but the three effects may be clearly separated.

(1) *The Effect of Ammonia.*—The effect on the viscosity of a latex of the addi-

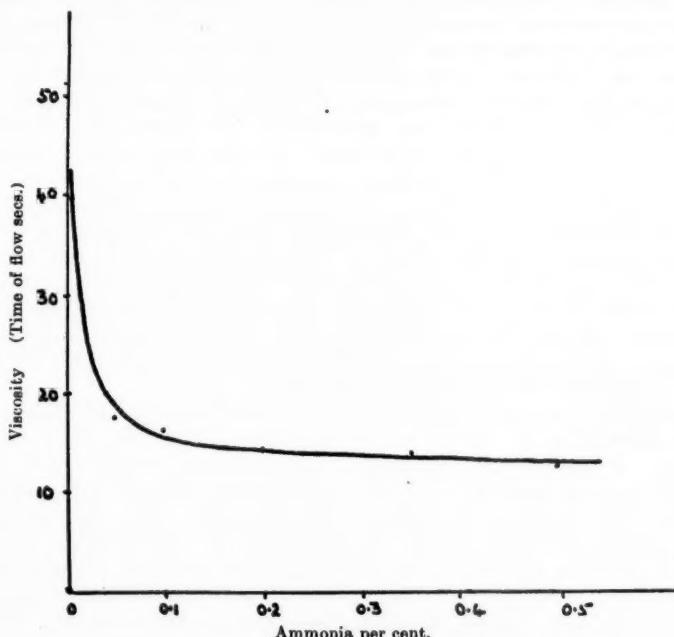


Figure 5—Effect of Alkalinity on Viscosity

tion of ammonia is striking. The general path of the change is shown in Fig. 5 for a simple latex mixing. The curve for an uncompounded latex has the same characteristics.

The viscosity falls sharply up to approximately 0.05 per cent and still decreases up to an ammonia content of 0.10 per cent. Thereafter the diminution is small and mainly attributable to dilution. The reason for the change is probably this. The change on the particles which corresponds to a double layer potential of approximately 0.035 volt, is affected considerably by the alkalinity of the latex. Consequently, at neutrality where the charge is small, not zero because the iso-electric point is at a p_H of approximately 4.2, the particles approach each other more closely, and their mutual effect is high. As the charge increases, the repulsion increases, the mutual interaction of the particles decreases and the viscosity falls. The higher the dilution the smaller the effect.

The necessity for controlling the ammonia content in view of its effect on viscosity has been found of particular importance in the centrifuging of latex, where it is found that there is practically no difference in the efficiency of separation between the limits of 0.10 per cent and 1.00 per cent ammonia, but if the ammonia is raised from 0.05 to 0.10 per cent the efficiency of separation is substantially increased. (British Patent 319,410 (1928).)

The Addition of Ionic Coagulants or Sensitizers

If it is assumed that these are without effect on the solvation of the adsorption layers, the discharge of the particles by oppositely charged ions should increase the viscosity. The result is as anticipated, the addition of such substances leading to heavy thickening and finally to coagulation. This effect has been utilized to produce creams or pastes for commercial use; in patents (British Patent 223,263 (1923)) where the sensitizing and thickening agents are acetic or formic acid or solutions of salts; (British Patent 312,947 (1928)) where zinc oxide is the active agent, and (British Patent 326,210 (1928)) where sodium silicofluoride is used.

(2) *Modification of the Nature and Amount of the Adsorption Layer.*—This can be done in a number of ways. The hydration of the adsorption layer can be reduced by the use of small quantities of dehydrating agents or by heat treatment with a consequent diminution in viscosity. On the other hand, by treatment with such materials as albumen, casein, and hemoglobin, which are themselves heavily hydrated, the viscosity is strongly increased. A large number of materials have been proposed and many of them patented for the thickening of latex in this way. Among them may be mentioned hemoglobin and zinc oxide (British Patent 301,077 (1927)) casein, egg and blood albumen, sodium silicate (British Patent 235,888 (1924)) blood (British Patent 279,336 (1927)), plant extracts (British Patent 291,-805 (1927)), and milk (British Patent 277,194 (1926)).

An outstanding example of the effect of heavy hydration of the protective envelopes is afforded by the special case of flocculated rubber precipitates prepared from latex. In the method according to British Patent 373,262 (1931) sodium silicate, for example, is added to latex in a state of high dilution and an aluminum salt added. The rubber is precipitated simultaneously, with the formation of heavily hydrated aluminum silicate which protects the agglomerates. The particles of the resulting material, which outwardly resembles latex, though on closer inspection is seen to be finely granular, are so heavily hydrated that on filtration a highly viscous paste is obtained resembling face cream in its consistency, which yet has a concentration of only 20 per cent. Needless to say, such a material is very stable in view of its protection and the fact that the particles have already undergone a coagulation process.

The foregoing will explain more clearly what was meant by the statement, that other than by direct concentration or, on the other hand, dilution it is not easy to alter the viscosity of a latex without affecting its stability.

A note should be interpolated here concerning the action of caustic alkalis. It has been indicated previously in the case of ammonia that to raise the alkalinity is to increase the charge and thereby to reduce the viscosity of a latex. *A priori* one would expect the same of a caustic alkali. Such is, however, not the case, or though an increase in charge is obtained, the more powerful action of the caustic alkali on the protein layer in general leads to a slight thickening of the latex.

Before leaving the subject of the viscosity of latex, mention should be made of the phenomena covered by the word thixotropy.

Freundlich (*J. Soc. Chem. Ind.*, **39**, 222T (1934)) has given a simple definition of

thixotropy. "A material is said to be thixotropic if when at rest it becomes solid but liquefies again on shaking, the process of solidification and liquefaction being reversible and capable of being repeated at will." In other words, a thixotropic material is one which may be transformed from a thick gel or gel-like state to a fluid state by shear, regaining its gel-like form some time after the shearing forces are withdrawn.

It will therefore be seen that thixotropy is really the extreme case of the phenomenon of structural viscosity. Dispersions of many substances, particularly of certain clays, such as bentonite, have this property; it is also well known in the paint industry. Many latex compounds, particularly certain thickened latices and compounded high concentration latices, show this phenomenon. Use has been made of this phenomenon in (British Patent 342,469 (1928)) in which such materials as bentonite clay, and lithium sulfate are added to latex to give it a pronounced thixotropic behavior. The treated latex is then used, for example, for dipping processes, a thick layer of temporarily gelled latex being removed on a former withdrawn slowly from the mixing, though the latex is fluid to the rapid introduction of the former.

Surface Tension

The second physico-chemical property of latex that warrants examination is that of surface tension. The study of surface forces as applied to latex may appear somewhat academic, but on closer examination its importance as applied to manufacturing processes is surprising. Surface tension is related to such things as wetting properties, penetrating power as regards textiles, froth formation and stability, air bubble removal and persistence.

The only methods that are reliable for the measurement of the surface tension of a latex are those depending on the detachment of some form of frame from the surface of the dispersion, the best known and most convenient form being the de Nouy instrument.

Here the force required to detach an annular ring from the surface is recorded in terms of the torsion of a wire. The ring, approximately 2 cm. in diameter, is suspended from a stirrup, the force necessary to detach it being provided by the torsion wire to which the arm carrying the stirrup is clamped. The reading on the graduated torsion head gives a measure of the surface tension, provided this has previously been calibrated with a liquid whose surface tension is known. Alternatively the pointer may be brought back to zero by means of weights. The apparatus is quick and convenient to use and to clean, and gives reliable and reproducible results except for viscous mixings or latices. With viscous latices the time of detachment of the ring is long, and it is difficult to tell when detachment begins as film drainage is protracted. Other methods for the determination of the surface tension of latex, such as those depending on bubble detachment, do not give reliable or interpretable results. An examination of recent samples of centrifuged latex of 60 per cent concentration and 0.5 per cent alkalinity gave a surface tension of 42.3 dynes per cm. at 19.3° C. That of a normal 38 per cent latex is somewhat lower than this, and varies slightly from latex to latex, while that of 60 per cent is fairly constant. Hauser and Hünemorder (*Trans. Inst. Rubber Ind.*, 8, 321 (1932)) give the following respective figures for centrifuged normal latex, and Revertex diluted (presumably with distilled water) to 20 per cent concentration, 42.75, 39.50, 37.00 dynes per cm.

The relation between these figures is understandable. Revertex has the lowest value on account of the higher content of soaps and surface-active substances pres-

ent, due to its mode of manufacture and preservation. On the other hand centrifuged latex, due to its mode of preparation, undergoes a separating or purifying process wherein a part at least of the surface-active substances naturally present are removed. This accounts for the higher surface tension value found for the centrifuged material, and means that in its un compounded state, and probably often when compounded, centrifuged latex should show a reduced tendency to froth and to entrap and retain air, an important point in the commercial handling of the material.

The nature and quantity of the serum components of a latex vary with the age of the tree, with the weather conditions, and the time when the latex is collected; consequently, the surface tension also alters somewhat in keeping with these variations as the amount of surface-active substances present will vary with these factors.

The first question arising in connection with surface tension concerns the treatment of textiles with latex.

In connection with the impregnation with latex of woven, twisted, or spun fibers, it must be realized that the mechanical interstices are capillaries, and the successful filling-up of narrow capillaries with latex depends on the viscosity of the fluid forced into the capillaries and the means whereby this is overcome, the size of the particles of the suspension that it is desired to get into the capillaries, and the way in which the capillaries are wetted by the aqueous medium carrying them. Finally, as far as the commercial use of the product is concerned, consideration must be given to the manner in which the rubber deposited adheres to the fiber itself. The particles of commercial latices have on an average a diameter of approximately 1.5μ , measured with the microscope. Probably their effective diameter is much larger in view of their negative charge and the fact that the capillaries into which they are being induced to enter are similarly charged. Obviously latex rubber can only penetrate into spaces between fibers of sufficient size to admit particles of the effective diameter of the latex particle. Hence, apart from considerations connected with surface tension, to obtain a good impregnation, the particles must be kept as small as possible. The particles of the latex must not agglomerate in any way, as thereby their effective diameters are increased and their penetration is poor; that is, the latex must be stable. The presence of a coagulant, either in the latex or in the fibers, prevents their satisfactory impregnation.

The rubber particles in the skim of centrifuged latex are smaller than those of the 60 per cent cream. An estimate under the microscope gives an average particle size of $\frac{1}{2}\mu$ - $1\frac{1}{2}\mu$, compared with that of 1.5μ for the latex cream. This skim has been suggested as being particularly suitable for the impregnation of textiles. (Crockett, *Rubber Age* (N. Y.), 1934, 235). It has also been claimed that dispersions of Du-prene contain similarly small particles. Trials have shown that, using preserved skim latex for soaking, good results are obtained for the adhesion to cord fabric, particularly if the fabric is first of all treated with a suitable wetting agent.

The passage of fluids through capillaries depends on the viscosity of the fluid and on the pressure head. Hence to obtain rapid impregnation it is desirable that the viscosity of the latex mixing be low, that is, for impregnation purposes it is preferable to dilute the latex to a concentration, for example, in the neighborhood of 25 per cent. The use of a positive hydrostatic pressure or a negative one (*i. e.*, a vacuum) is also found to assist the rate of penetration and has been described in British Patent 316,335 (1928); 361,398 (1930); (Head), British Patent 391,031 (1932); (Duary Serra), British Patent 408,931 (1932); (Brandwood), U. S. Patent 1,411,786 (1922); (Hopkinson), U. S. Patent 1,424,020 (1922).

Lejeune and Bongrand (British Patent 338,381 (1929); 344,414 (1929); French

Patent 700,850; 700,851; 700,852 (1929)) on the other hand, worked in the other direction. Instead of grappling with the problem of getting latex particles into the small interstices of textile materials, they impregnated the fibers at a stage when the interstices were not small, that is, in the roving stage and claim improved results.

The physico-chemical methods of improving the impregnation of textiles concern the wetting and indirectly the charge on the fibers.

Uncompounded and untreated latex has a surface tension in the neighborhood of 42 dynes per cm. As far as wetting properties are concerned, this is high, that of benzene, being, for example, 29 dynes per cm. The soaps and protective agents used in the compounding or concentrating of latex tend, however, to reduce this figure. The wetting properties of a latex are, however, so important that if these are wrong, no amount of ordinary mechanical force or treatment will mend matters, and on the ease with which the latex wets the material under treatment depends the speed and hence the commercial value of the process.

In the textile world a number of wetting agents are used extensively in the treatment of fibers and fabrics. These are substances which, when added in small quantities, reduce the interfacial tension and angle of contact with respect to the fiber very considerably. They act similarly in the case of latex. The surface tension of latex to which 5 per cent of wetting agent on the rubber content has been added, have been given by Hauser and Hünemorder (*loc. cit.*) for 31 proprietary wetting agents. Latices containing a proportion of such wetting agents wet fibers and fabrics more rapidly and effectively than untreated latices. At the same time these wetting agents cannot possibly alter the actual diameter of the penetrating rubber particles, though by modifying the charge on the fibers and possibly on the rubber particles they alter to some extent their effective diameters. It is, however, claimed that they have the effect of opening up the fibers.

Most of the wetting agents are stabilizers for latex, and therefore tend to keep the individual latex particles discrete, which is a good point, but this very virtue, in view of the fact that in general the wetting agents must be added to the latex tends to upset subsequent coagulation, and hence in some cases processing is made difficult. It has also been mentioned by Hauser and Hünemorder that Igepon T has somewhat different properties, in that good results are obtained if the textile is first of all treated with it and subsequently processed with latex. This method obviates the difficulties that may be associated in some processes with the stabilizing effect of the wetting agent in the latex.

The use of wetting agents with mixings of coarse particle size, or wherein the particles have agglomerated, in general, only serves to accentuate the filtering out of the particles by the textile material, as the serum wets the textile more rapidly, leaving the rubber behind.

For the treatment of loose fibrous masses in bulk, such as carded wool, cotton, felt, and the like, improved results are usually obtained with the use of wetting agents in the latex. Whereas the interfacial tension may be reduced by the use of wetting agents as described, improved results may also be obtained by treating the fibers themselves as well as the latex. The wax present in cotton fibers is the chief contributor to defective wetting, and a definite improvement is obtained if the fiber is first of all scoured with a solvent to remove such materials before treating with latex. The treatment of the fiber with caustic soda prior to the treatment with latex has also been claimed as an advantageous process. It is known that mercerizing processes reduce the charge on the fiber, and it is possible that any improved results that are found may be partly connected with this effect.

The treatment of textiles with rubber solution has not only the advantage of the micellar structure, but also of the solvent of low surface tension and its scouring

action on the waxes of the cotton. On the other hand, rubber solutions used for the impregnation of fabrics necessarily contain less rubber in view of their viscosity, and with their use as high an impregnating weight cannot be obtained as with latex. As far as frictioning and topping processes are concerned, impregnation before vulcanization is very small, but after very good flow of the rubber and smearing of the fibers taking place during cure. In the case of latex, there is little change between the degree of penetration before and after cure. The difference between the two processes is sufficient to make one realize that there are differences between the adhesions of the rubber and fiber in the two cases.

It is one thing by the use of wetting agents to make the aqueous serum wet, but it is quite another to ensure good contact between the fiber and the rubber itself, that is, good wetting of the fiber by the rubber. It will, therefore, be understood that up to a point it is beneficial and important to improve the serum wetting by all possible means, but there is still a considerable amount of work to be done on the question of improving the wetting of the fibers by the rubber.

As far as latex is concerned, a low surface tension generally goes hand in hand with an increased tendency to entrain air bubbles. The presence of froth-forming substances usually implies a reduced surface tension. From this point of view the more stable latices and those with low surface tensions are less desirable for dipping and spreading purposes where a relatively high viscosity and solid content are required. To assist the entraining of air, froth-forming substances must be present, giving rise usually to a reduced surface tension. In certain cases, on the other hand, it has been suggested that the addition of small quantities of electrolyte assists the removal of air bubbles from mixings and at the same time raises the surface tension.

In discussing the question of the entrainment of air bubbles, one's thoughts turn immediately to what is perhaps one of the most important of all latex processes, namely, that which is adopted in the production of Dunlopillo material. This is, of course, a special type of sponge rubber made from latex, which is produced by mechanically aerating a treated latex mixing, setting and vulcanizing the resulting foam. In this process rapid frothing and a stable foam are very desirable. The frothing operation is usually carried out by mechanical beating, as in the whisking of the white of an egg. A reduced surface tension is obtained by the addition of a suitable soap solution. However, such a complex system as a froth or rather a dispersion of air distributed in an equally complex system such as a latex mixing does not depend merely on surface tension for its realization or control. The viscosity of the froth, the viscosity of the surface films which is very different from that of the bulk mixing also play their part in the process. It is likely that for a true understanding of this process information is required about the surface tension immediately the surface is formed, i.e., what may be called the dynamic surface tension. It is probable that this quantity, which differs from the static surface tension (that of a clean but old surface), comes strongly into play in the formation of fresh surfaces as in the frothing process.

The compounding ingredients themselves have a very powerful influence on the surface tension of a latex, and as might be expected, on a stable froth obtained from a latex mixing. Of these, zinc oxide has perhaps one of the most pronounced and characteristic effects. The influence of gelling or setting agents is again very interesting to examine, particularly in view of the fact that froths in which setting agents are incorporated show a big change in structure as the system sets. It is observed, for instance, that the bubbles in an average latex froth before setting are about 0.1 mm. in diameter. When the froth sets, the bubbles increase to about 1 mm. in diameter, practically the whole change taking place at the instant of setting which is very sharp. Such a change indicates a sudden and very large change in

surface forces. The actual change in surface forces is very difficult, if not impossible, to follow with apparatus at present available.

Another rather interesting effect, and one difficult to explain, is the deleterious effect on a latex froth of particles in the surface. The addition of powders in general makes frothing more difficult, and necessitates increased amounts of soap to produce a good froth. Prolonged frothing until the rubber coagulates to fine particles invariably breaks the froth, though no additions to the mixing have been made. The actual influence of the latex particles themselves on the surface tension is difficult to assess. Perhaps for a concentrated mixing they do have a definite influence. Unfortunately the surface tension of a concentrated and therefore viscous mixing is very difficult to measure, and no data exist. It is difficult to believe that the attractions between the latex particles, which are rarefied compared with the molecules of the serum, can have any pronounced influence on the cohesive forces of the surface layer. The way in which they adsorb at their surfaces is another matter. Such an opinion is supported by Shacklock's observations (*Trans. Inst. Rubber Ind.*, 6, 259 (1930)), that the surface tensions of benzene rubber solutions are to all intents and purposes the same as those of the solvent itself.

Stability

Stability is closely linked with surface tension and viscosity. What properties characterize a stable latex? A stable latex on exposure to frictional forces, such as rubbing or grinding, does not readily ball up or form lumps of coagulated rubber, and when treated with small quantities of known coagulants it exhibits little outward change, and the coagulum subsequently formed from it is in general friable and short. An unstable latex on the other hand behaves in quite the opposite manner. It is sensitive to friction or mechanical action such as rubbing or stirring, and forms clots or coagulates readily when treated with coagulants. The coagulum obtained from it is strong and coherent.

The stability of a latex depends intrinsically on the mutual repulsion of the particles due to charge or by protective envelopes. The measurement of latex stability is a subject that has been under careful examination for a long time, but the results of the work carried out are only now being systematized. The main difficulties that have had to be contented with are those associated with the determination of an end-point, and the fact that a measurement which is significant for coagulating or gelling processes is not necessarily so for those in which the latex has to undergo mechanical action or is subjected to friction. For example, a latex mixing after beating to a froth needs a more reduced amount of gelling agent in order to cause it to set than does the same mixing in the unbeaten condition. The difference is due partly to the mechanical treatment of the latex and also to the destabilizing effect of the dispersed air. Again, gelling times for fresh latex appear to bear no relation to the running times of the concentrating centrifuges before clogging sets in.

Until recently for experienced workers, the hand rubbing test has been a good standby as a rough-and-ready method of assessing the stability of a latex mixing, the combined friction and heat of the hand with consequent drying out influencing the end-point. It is evident from these few observations that stability and its measurement has still to receive considerable investigation.

Acknowledgment

In conclusion, the author wishes to express his thanks to the Dunlop Rubber Company for permission to present this paper, and to various colleagues and friends for suggestions and assistance.

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Heat Changes in the Vulcanization of Rubber

I. Qualitative Tests on a Comparative Basis

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Introduction

That the vulcanization of rubber by sulfur is a peculiar exothermic reaction has been reported by various investigators, among whom Williams and Beaver (*Ind. Eng. Chem.*, 15, 255 (1923)) obtained heating curves of the vulcanization of rubber containing three different proportions of sulfur, and noticed that the heat evolved increased with an increase in the proportion of sulfur used, but that the time required to reach the maximum temperature remained nearly constant. According to Perks (*J. Soc. Chem. Ind.*, 45, 142 (1926)) an increase in the internal temperature of rubber samples was the greatest in samples compounded with 20 per cent of sulfur, and the heat evolution became less with more sulfur, the time required to reach the maximum evolution of heat varying somewhat with the amount of sulfur.

Toyabe (*J. Soc. Chem. Ind., Japan*, 33, 288 (1930)) reported that the maximum evolution of heat, when heated in nitrogen gas, increased with an increase in the proportion of sulfur, and the time required to reach the maximum temperature was nearly constant; about one-half of the total sulfur at this time was found to be combined, and this ratio was not affected by a change in the amount of sulfur or by a change in the temperature of vulcanization.

Hada and Nakajima (*J. Soc. Rubber Ind., Japan*, 5, 288 (1932)) studied the heating curves of rubber compounded with 3, 5, 10, 15, 20, 25, 30, 35, 36, 38, 40, 45, 50, 60, and 70 parts of acid-free sulfur per 100 parts of standard smoked sheet. The extent of heat evolution increased with an increase in the proportion of sulfur added, until a theoretical saturation point of sulfur in the rubber was reached, and the time at which the initial exothermic reaction appeared was nearly alike in all samples, and it was not influenced by a change in the proportion of sulfur added. There was but one exothermic phenomenon in the vulcanization reaction.

As to the effect of resins and proteins on the vulcanization reaction, Stevens (*Kolloid Z.*, 14, 91-96 (1914)) reported that the vulcanization coefficient of pure raw rubber was far lower than that of untreated raw rubber, while resin-free raw rubber gave somewhat lower values in his studies of the vulcanization coefficient of resin-free rubber and pure rubber with or without the addition of various resins, nitrogenous substances and others compounded with sulfur. Dubosc (*J. Soc. Chem. Ind.*, 36, 296 (1917)) also noticed that it was difficult to vulcanize rubbers containing no insoluble substances and resins. According to Perks (*loc. cit.*) the maximum temperature on the heating curve was greater with resin-free rubber than raw rubber but the time required to reach this point was also longer when the samples were compounded with 30 per cent of sulfur.

An attempt was made by the authors to ascertain in a quantitative way the effects of various compounds contained in the raw rubber on the vulcanization

reaction. The following experiments include the qualitative studies in connection with this object.

Experimental

1. Samples—

(a). *Raw Rubber*.—It was prepared by milling standard smoked sheet for 10 minutes and pressed to 0.25 mm. thickness by passing through a mill with rolls 30 cm. long and 15 cm. diameter, with a surface temperature of 60°, and with a rotating ratio of 1.3.

(b). *Resin-free Raw Rubber*.—It was prepared by extracting finely cut milled samples in acetone for 20 hours and, after the removal of acetone-soluble matter, drying *in vacuo*.

(c). *Pure Rubber*.—Endō's method (*J. Soc. Chem. Ind., Japan*, **35**, 7 (1932)) was used. One per cent milled raw rubber prepared as above (a) was dissolved in benzene, filtered several times, and when the filtrate became nearly clear it was precipitated by adding a sufficient quantity of 97 per cent alcohol to make a silky looking precipitate, which was dried *in vacuo* after filtering off the alcohol.

Samples (b) and (c) were kept in acetone and in darkness in order to prevent the effect of air and sunlight, and these were dried in a vacuum desiccator, avoiding sunlight.

To 100 parts of the above samples, 5, 10, 15, and 20 parts, respectively, of acid-free sulfur were added, and the samples were milled at room temperature.

2. *Apparatus*.—Around the mercury bulb of a long thermometer which was graduated to 0.2°, 50 grams of sample of 0.25 mm. thickness was wrapped in a cylindrical form of 3 cm. diameter and 8 cm. long. It was then covered with cloth and placed in a glass tube of 3.8 cm. inner diameter and 19.5 cm. long. The space between the sample and the glass wall was filled with talc, which was previously heated to 160° for a long time. All samples were treated in the same way (see Figure 1). It should be noted that a loss of heat and oxidation in contact with air may happen in this case, as indicated elsewhere by Toyabe and Furukawa (*J. Soc. Chem. Ind., Japan*, **32**, 1100 (1929)) and Hada (*J. Soc. Chem. Ind., Japan*,

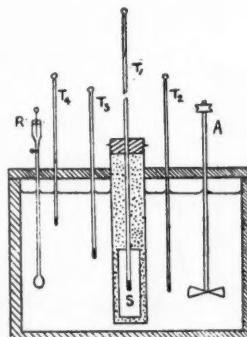


Figure 1

ANALYTICAL DATA

	Mixtures Rubber Part	Sulur Part	Acetone Extract %	Free Sulfur %	Com- bined Sulfur %	Sulfur Found %	Used in Com- pounding %	Loss of Sulfur %
Raw rubber	100	5	2.50	1.80	2.40	4.20	4.76	0.56
Raw rubber	100	10	4.25	3.75	5.00	8.75	9.09	0.34
Raw rubber	100	15	6.00	5.23	7.15	12.38	13.04	0.68
Raw rubber	100	20	8.62	7.35	9.10	16.45	16.67	0.22
Resin-free rubber	100	5	2.82	2.42	2.05	4.47	4.76	0.29
Resin-free rubber	100	10	4.75	4.28	4.10	8.38	9.09	0.71
Resin-free rubber	100	15	7.35	6.88	5.85	12.73	13.04	0.31
Resin-free rubber	100	20	10.21	9.22	7.21	16.43	16.67	0.24
Pure rubber	100	5	2.75	2.56	2.17	4.73	4.76	0.03
Pure rubber	100	10	4.56	2.40	4.63	9.03	9.09	0.06
Pure rubber	100	15	7.88	7.55	5.05	12.60	13.04	0.44
Pure rubber	100	20	12.18	11.05	5.55	16.60	16.67	0.07

34, 64 (1931)), but these effects were disregarded, since this was a comparative test.

3. *Method of Determination.*—A castor oil bath of 24 cm. diameter and 15 cm. deep was kept at $160 \pm 0.2^\circ$. A glass tube containing the sample was immersed in the bath quickly to a depth of 14 cm., and the reading of the thermometer was made every minute to obtain a heating curve. When the glass

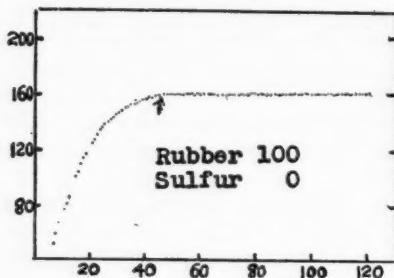


Figure 2

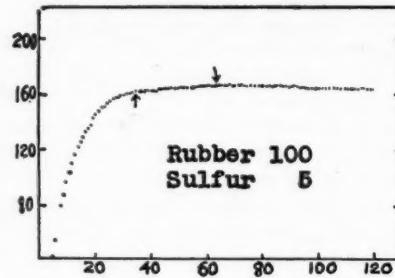


Figure 3

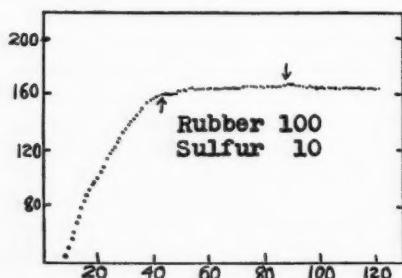


Figure 4

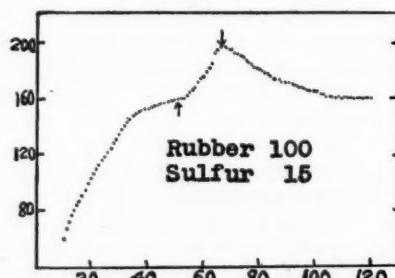


Figure 5

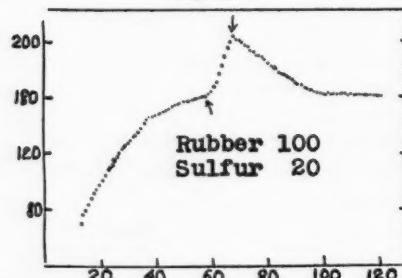


Figure 6

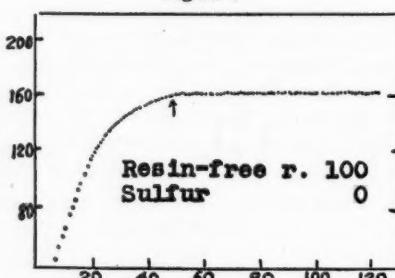


Figure 7

tube was immersed in the bath, the temperature of the bath at the thermometer T_2 showed a lowering of 1° , but it returned to normal within 3 minutes.

4. *Analysis of Sulfur in the Products of Heating.*—In order to ascertain the relation between the heating curves and the free and combined sulfur contents of the products of heating, the sulfur in these products was determined by the method of Water and Tuttle (cf. Weber, "Chemistry of Rubber Manufacture," 1926).

The results of the experiments are shown in the following diagrams. The values on the abscissae are the time (in minutes) and those on the ordinates are the temperatures (Centigrade).

Experimental Results and Discussion

With the samples and apparatus as described above, and as shown in Figs. 2 to 16, it was noted that:

- (1) there was practically no exothermic or endothermic reaction in samples without sulfur;
- (2) those samples containing sulfur gave an endothermic reaction at the melting

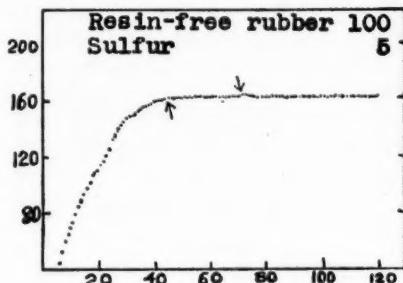


Figure 8

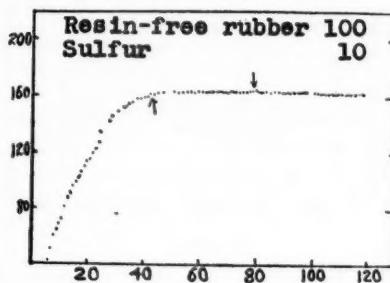


Figure 9

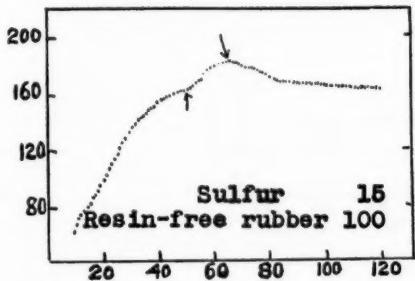


Figure 10

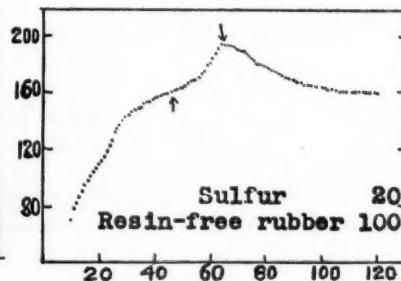


Figure 11

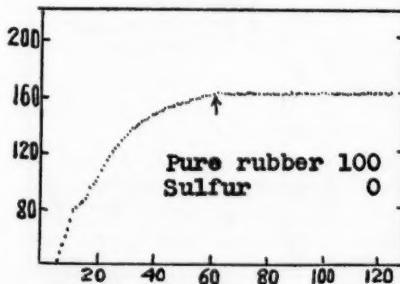


Figure 12

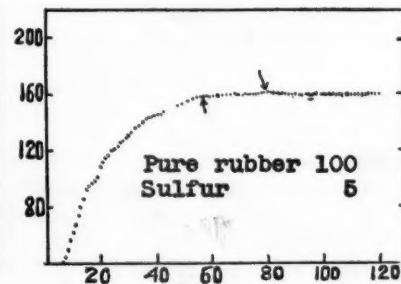


Figure 13

point (119°) or transition point of sulfur (the extent of this reaction was, however, not sharp, probably due to rapid heating);

(3) after reaching the temperature of the bath, there was an immediate exothermic reaction, the maximum temperature was reached, and then the system gradually returned to the temperature of the bath—(compare these 3 systems in Figs. 17 and 18);

(4) the maximum temperature was the highest in the raw rubber system, the

resin-free rubber system showed the next highest temperature, and the pure rubber system—the lowest temperature;

(5) the time to reach the maximum temperature was the longest in the pure rubber system, the shortest in the resin-free rubber system, while the raw rubber

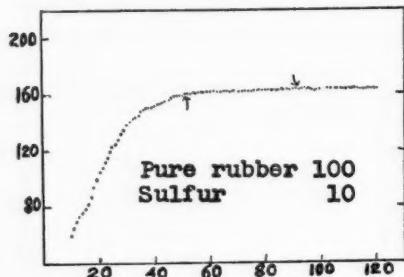


Figure 11

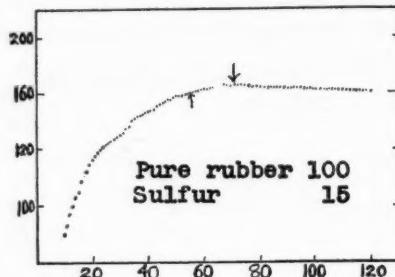


Figure 15

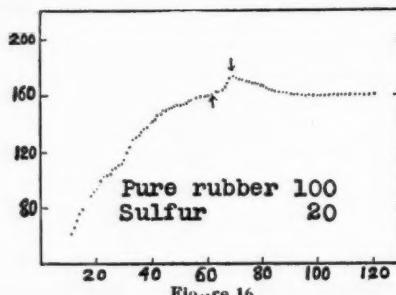


Figure 16

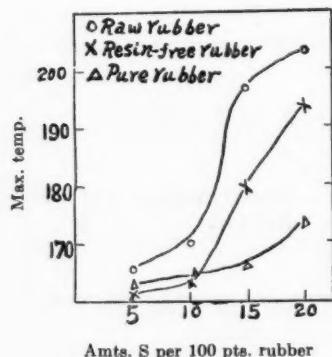


Figure 17

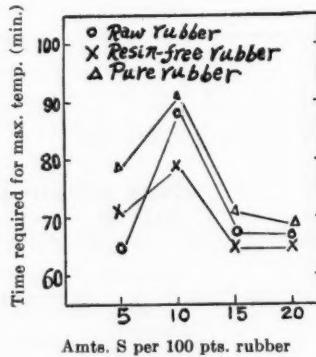


Figure 18

system came between these two; in general it was shortened by increasing the proportion of sulfur, but the mixtures with 10 per cent sulfur required a longer time in all systems;

(6) samples free of resins and nitrogenous substances were slower to vulcanize than samples free of resins only (Fig. 18), but the former had a higher combined

sulfur content (Fig. 19) up to 10 per cent of added sulfur, and the elevation of temperature by the vulcanization reaction was also higher (Fig. 17);

(7) the samples free of resin and nitrogenous substances gave less combined sulfur when more than 10 per cent of sulfur was added, and they required a longer time to reach the maximum temperature in comparison with the two other systems;

(8) it was a noteworthy fact that, when the added sulfur was less than 10 per cent, the samples containing no resin or nitrogenous substances had more combined sulfur than did the samples free of resins only;

(9) the sulfur required for the compounds $(C_6H_5)_{10}S$, $(C_6H_5)_9S$ and $(C_6H_5)_8S$, respectively, is 4.99, 4.97, and 5.55 per cent. For combination of sulfur to these extents, the presence of nitrogenous substances may be rather detrimental, but these substances may be necessary for the combination of sulfur above such amounts. The cause of this phenomenon may be due either to the presence

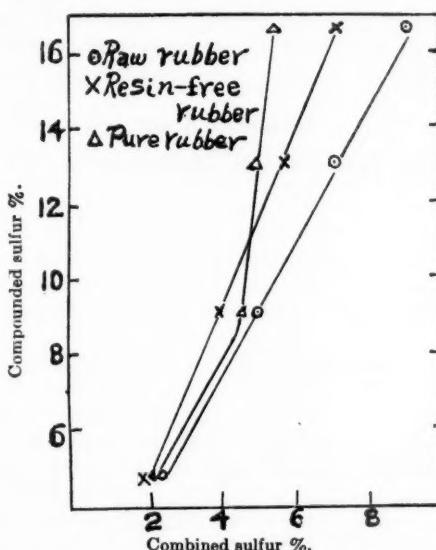


Figure 19

of a step in the combination of rubber hydrocarbon and sulfur at approximately the above formulas, or to an accelerating effect of the nitrogenous substances. The latter reason seems the more probable one, and

(10) though there are several theories to explain the mechanism of acceleration of vulcanization by the resins or nitrogenous substances, it is generally accepted by other investigators and by the authors that, judging from experiments, it seems that the substances which accelerate vulcanization are not resins but are more likely the nitrogenous substances.

Summary

As a preliminary test of the quantitative determination of the thermal changes in the vulcanization of rubber by sulfur, 100 parts of raw, resin-free and pure rubber were compounded with 5, 10, 15, and 20 parts sulfur, respectively, and vulcanized in a thermostat at $160 \pm 0.2^\circ C$. The change in temperature was noted

by reading a thermometer, the mercury bulb of which was inserted in the center of the sample, and the heating curves thus obtained were compared with the analytical results of free and combined sulfur determinations.

1. There was practically no exothermic or endothermic reaction in the samples without sulfur.
2. Those samples containing sulfur had but one maximum exothermic point, and the maximum temperatures decreased in the order: raw rubber system > resin-free rubber system > pure rubber system.
3. The times required to reach the maximum temperature decreased in the order: pure rubber system > raw rubber system > resin-free rubber system.
4. The time required to reach the maximum temperature was shortened by increasing the proportion of sulfur added, except for the 10 per cent mixtures.
5. The presence of nitrogenous substances was detrimental to the vulcanization process, in the reactions where less than 5 per cent of combined sulfur was obtained, but their presence was necessary to obtain more combined sulfur.
6. The agent which accelerates the vulcanization reaction seems to be the nitrogenous substances.

Acknowledgment

Thanks are due to M. Yasushi and M. Matsumura for their help in the experiments.

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The Raman Spectrum of Rubber

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It has been previously reported that the Raman effect is exhibited by rubber as a continuous scattering together with the presence of broad bands (Franklin and Laird, *Phys. Rev.*, **36**, 147 (1930); Busse, *J. Phys. Chem.*, **36**, 2862 (1932)). Busse attributed this result to the viscosity of the solutions or to the possibility that the rubber groups respond to a wide range of frequencies. However, viscous solutions of polystyrene in carbon tetrachloride give a line spectrum (Signer and Weiler, *Helv. Chim. Acta*, **15**, 649 (1932)). As to the second explanation, this does not seem to be the nature of the Raman effect (Bär, *Helv. Phys. Acta*, **4**, 369 (1931); Bär, *Z. Physik*, **79**, 455 (1932)). The Raman effect has been investigated extensively for terpenes other than rubber.

The bands and continuous background for rubber appear to be due to fluorescence of impurities, oxidation products, or the rubber hydrocarbon. The acetone extract of rubber is fluorescent as observed in ultra-violet light. The intensity of the bands and background for rubber decreases as the rubber is purified. However, acetone extraction and two diffusions with ethyl ether did not remove the fluorescence entirely, as could be seen by examination between complementary light filters. Some of the background is undoubtedly unmodified radiation, that is, Tyndall scattering by the colloidal structure and by motes. This can be reduced by a monochromatic light filter.

In contrast to the previous results a line spectrum has now been observed for rubber. Gels made with diffusion rubber (Memmler, "Science of Rubber," Am. Ed., Reinhold Publishing Corp., New York, 1934, p. 174) give Raman lines of sufficient intensity to be seen against the background. A mixture of 43% carbon bisulfide and 57% carbon tetrachloride is suitable as a solvent, since this mixture has about the same refractive index as rubber and has a simple Raman spectrum. Carbon tetrachloride has been used alone with petroleum ether diffusion rubber. Concentrations of rubber used were from 10 to 40% by volume. The preparations were clear, colorless gels, free from any gross optical imperfections. They were protected from ultra-violet light by being completely surrounded by a filter solution. They did not show any perceptible darkening due to the exposures. The Raman lines were excited by the 4358 Å. U. mercury line.

The three most intense Raman frequencies for rubber are 1672, 1460, and 1382 cm.⁻¹. Isoprene has frequencies of 1640, 1426, and 1388 cm.⁻¹ (Dadieu and Kohlrausch, *J. Opt. Soc. Am.*, **21**, 286 (1931); Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932)). Thus the 1640 frequency for isoprene, ascribed to the double bond, is smaller than the corresponding frequency in rubber. However, trimethylethylene has three frequencies which agree closely with these most intense lines for rubber. Thus the Raman spectrum data appear to confirm the generally accepted views regarding the chain structure of rubber, although a cyclic structure is not definitely excluded, since cyclic terpenes have a spectrum of this nature.

The group of lines at 2900 cm.⁻¹, characteristic of the aliphatic C—H linkage, can be observed readily for rubber. Measurements of the fainter lines for rubber will be possible with further reduction in the background intensity.

[Translated by Chas. Blanc for Rubber Chemistry and Technology from the Journal of the Rubber Industry (U. S. S. R.), Vol. 10, No. 1, pages 28-33, January, 1934.]

Elastic Hysteresis and Increase in Tensile Strength at Low Temperatures

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The nature of elastic hysteresis is one of the most interesting and least investigated problems of rubber. The loss of energy in elastic hysteresis is closely connected with the shock-absorbing properties of rubber, which constitutes a practical aspect of this problem. By elastic hysteresis is commonly understood the energy capacity of the process of stretching and contraction, and this is measured quantitatively by the area between the elongation and contraction curves (Fig. 1). The absorbed energy is expended in internal friction and in overcoming the forces of cohesion between the irregularly distributed particles of the rubber coagulum, as well as those between the particles of rubber and filler in a compounded mixture. It should be emphasized that the Joule effect has no influence on the absolute magnitude of the elastic hysteresis, because in distinction to the latter it is thermodynamically a reversible process. In the study of the hysteresis loss on repeated stretching, Hock showed that the gradual decrease of the hysteresis loop after the first cycle confutes any attempt to explain elastic hysteresis by reversible structural changes during stretching and contraction. The increased hysteresis losses on addition of fillers to a mixture, and the definite quantitative relation with the reinforcing properties of fillers lead to the assumption that in this case only those processes can be considered as essential which take place at the boundary surface of rubber-filler. Experimental evidence shows that the optimum increase in the tensile strength of a mixture corresponds to the maximum hysteresis loss.¹⁴ The problem of the increase in tensile strength was most successfully studied by Wiegand,¹ who by the increase in strength effected by given ingredients implied the increased elasticity of the rubber mixture. According to him, the function A , representing elastic resistance, is equal to:

$$A = \int_{v_0}^{v_1} \int_{E_0}^{E_1} T dE dv$$

where T is the load, E is the elongation, and V is the filler in per cent by volume. A is represented by an area, and in a simple case, when the content of a filler is not varied, by an area below the curve of stretching between the coordinates:

$$A = \int_{E_0}^{E_1} T dE$$

An increment of this function ΔA serves then as an index of the reinforcing effect of an ingredient. A study of some fillers led Wiegand to the following conclusions. All fillers show an optimum capacity for increasing the tensile strength of rubber. This optimum becomes the more sharply marked the more multi-sided is the form of the particles of the ingredient. In general, an increased proportion of a filler results in a dilution of the rubber and a decrease of its ratio per unit volume of the mixture, with a consequent lowering of the ultimate elongation and elasticity. If,

however, a pigment possesses a highly developed surface and shows considerable cohesion with the rubber particles, it is capable of increasing the tensile strength of rubber up to definite volumes. By addition of barytes, whiting and lithopone, the cohesion increases at a slower rate than the decrease of the elastic resistance by dilution of the system. Carbon black and zinc oxide increase the tensile strength over wide limits, while magnesium carbonate and kaolin give sharply peaked curves of increased tensile strengths. Several authors, including Pickles,² Dawson,⁴ Wood and Speer,¹² Fromandi,¹⁰ Gowe,¹¹ Depew,⁶ and others, have shown the functional dependence between the reënforcing effect of an ingredient and the form and the size of its particles. Wiegand considers two forms of particles: "needle-like" and "spherical" particles. Needle-like pigments reach rapidly a maximum of surface saturation, *i. e.*, an optimum increase in tensile strength. Spherical pigments produce at the point of saturation a tetrahedral grouping, and this establishes an equality of the mutual distances and the retention of contact. Hock⁷

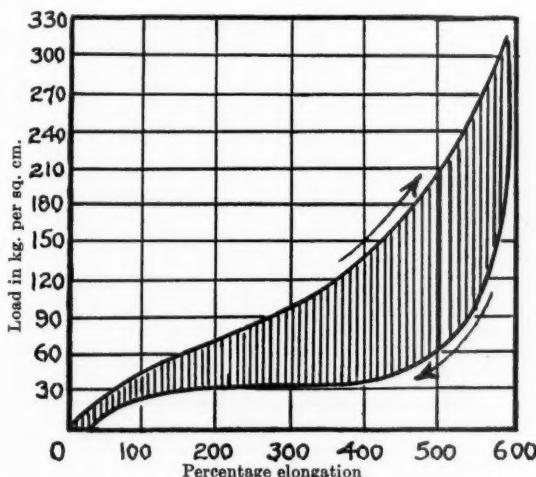


Figure 1

and later Boström³ and Grenquist⁸ advanced the highly suggestive idea that the reënforcement of rubber by ingredients is conditioned by the free surface energy of the system, a measure of which is the heat of wetting of the ingredient by the rubber. The rubber-filler system is basically a two-phase system, and therefore the free surface energy of the dispersed phase (the filler in this case) acts in all cases as the determinant factor. If we designate the total free energy of the dispersed phase by U , then $U = U_v + \sigma s$, or $\frac{U}{v} = \frac{U_v}{v} + \frac{\sigma s}{v}$, where U_v is the energy of the total volume, and σs is the excess free energy at the boundary layer. With increase in the degree of dispersion: s/v , the excess free energy $\frac{\sigma s}{v}$ increases. Therefore the more highly dispersed ingredients, which have a greater free energy, are more active and are capable of increasing the strength to a greater extent. The excess free surface energy is present at the boundary of any two contiguous phases. Adsorption is the result of decreased free surface energy, and therefore, according to the second law of thermodynamics, under isothermic conditions it proceeds spontaneously.

Only a part of the total surface of a filler comes in contact with the rubber, since wetting, because of agglomeration, cannot be complete. Thus there is a definite maximum loading, which when exceeded leads to an excessive overloading of the system and thus leads to a decreased wetting caused by the increasing agglomeration. The methods of thermochemistry make possible the determination of the heat of wetting of an ingredient by rubber. By analogy with molecular conductivity, it is possible by interpolation to introduce the concept of the heat of wetting U_c at an infinitely small loading. Then the relation is U_c/U_0 , where U_0 is the heat of wetting and $c =$ the rate of acting surface. Hock, who first proposed the concept of infinitely small loadings, calls a mixture with the heat of wetting U_0 an ideal one. Designating by A_0 the work of rupture of an ideal mixture, and by A_c that of mixtures with loading c , the increase in tensile strength can be determined from the relation: A_c/A_0 . It is necessary to note that the work

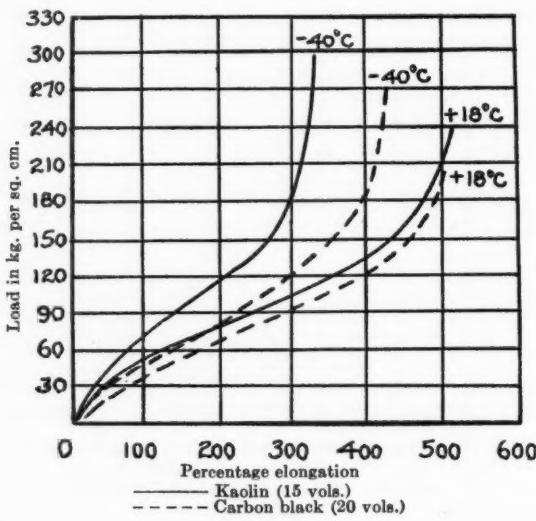


Figure 2

of friction enters into the value of A_c . The measurements show that $A_c/U_0 \approx 0.5$, hence only one-half of the total surface energy of tension is consumed in increasing the tensile strength of a mixture.

The purpose of the present investigation is to disclose the influence of low temperatures on the increase in tensile strength and elastic hysteresis.

Increase in Strength.—This was determined by the resulting elasticity, which was tested in a machine previously described.¹⁵ The experiments were carried out with the following ingredients: carbon black (GET), zinc oxide, kaolin (Turbov), whiting, magnesium carbonate, and lithopone, introduced into the master mixture in quantities of 5, 10, 15, 20, and 30 volumes. The master mixture was composed of (in parts):

Smoked sheet	100
Zinc oxide	5
Sulfur	2.5
Stearic acid	0.5
Mercaptobenzothiazole	0.6
Tetramethylthiuram disulfide	0.06

The results of the tests are given in Table I. These substantially confirm the data of Wiegand, though the ingredients in the present work possess lower reënforcing capacities because of the inferior dispersion of particles. The tests at lower temperatures showed an increase in elasticity (equal for the master mixture to 1092 under normal conditions and to 1126 at -40°); freezing resulted in optimum reënforcement, except with samples containing kaolin and carbon black in large proportions, for which a decrease of elongation was not compensated by an increase of load, because the stress-strain curve showed on freezing a characteristic rise at the point of rupture (Fig. 2). The same table shows that, on freezing, the optimum increase in tensile strength is shifted toward the smaller volume. The fact that a similar shift takes place also with whiting shows that the latter possesses a definite reënforcing effect, because such a phenomenon can take place only with reënforcing agents. The table also shows that lithopone is a typical inert filler.

Elastic Hysteresis Losses.—Cotton and Barron¹⁴ in their classical work on hysteresis based their investigation on the following concept of the work of rubber in stretching:

TABLE I
ELASTICITY OF MIXTURES WITH VARIOUS INGREDIENTS AT NORMAL CONDITIONS AND AT -40° (AT OPTIMUM VULCANIZATION)

Ingredients	5 Volumes		10 Volumes		15 Volumes		20 Volumes		30 Volumes	
	Normal Condition	-40°								
Zinc oxide	1171	1368	1470	1539	1627	1540	1000	1088	1009	1105
Kaolin	985	1100	974	1305	1272	1081	1025	972	748	902
Chalk	946	869	940	1085	975	1069	856	1040	758	794
Magnesium carbonate	1027	1162	1033	1380	1142	1254	761	1109	751	893
Lithopone	880	1170	789	1151	936	1203	935	..	762	948
Carbon black (GET)	1002	1255	1045	1123	765	691	771	711	444	..

$$\begin{aligned} A &= R + H \\ H &= A - R \end{aligned}$$

Further:

$$\begin{aligned} A &= (PE) + F_1 + Q \\ R &= (PE) - F_2 + Q \end{aligned} \left\{ H = F_1 + F_2 \right.$$

where A is the work expended in stretching, R is the work returned in contraction, H is the loss in elastic hysteresis, (PE) is the potential energy of elasticity, Q is the Joule heat, and F_1 and F_2 are frictional forces. With increasing stretching, the work expended and consequently the elastic hysteretic losses increased, since $H = A - R$. The latter equation shows that the maximum work expended, *i.e.*, the maximum increase in tensile strength, corresponds to the maximum loss in elastic hysteresis. Since $H = F_1 + F_2$, it follows that there is no filler which can reduce the elastic hysteresis losses in comparison with a pure mixture. The results of a large number of investigations showed that the loss in elastic hysteresis decreases rapidly with increasing temperature.

The purpose of the subsequent study was to explain the influence of low temperatures on the elastic hysteresis. The tests were carried out with the same fillers and the same technic.¹⁵ The method of investigation did not differ from that used with the Schopper apparatus, and is of no special interest. The results of the tests are shown in Table II. The hysteresis loop was taken at the point of rupture;

hence the absolute value of stretching, which differed for the various rubber mixtures, has no influence on the final results. It can be easily seen that for every ingredient there is a clearly defined relation between the volume loading, the work of stretching and the elastic hysteretic loss. The existence of a certain optimum volume (for carbon black 15-20, zinc oxide 15, kaolin 15, whiting 15-20, magnesium carbonate 15, and lithophone 15 volumes) is sufficiently clear, and requires no special explanation. An increase in the elastic hysteretic loss is in direct relation to the increased work of stretching, and at a normal temperature its optimum corresponds to the optimum increase in tensile strength for a given ingredient. In freezing, such a relation is not observed (Table II). In this case it is necessary to

TABLE II
LOSSES IN ELASTIC HYSTERESIS UNDER NORMAL CONDITIONS AND AT -40°

Ingredients	5 Volumes				10 Volumes				15 Volumes			
	Normal Condition		-40°		Normal Condition		-40°		Normal Condition		-40°	
	A	H	A	H	A	H	A	H	A	H	A	H
Carbon black	593	371	1027	490	878	437	973	536	1020	568	1160	614
Zinc oxide	328	130	336	138	376	178	424	200	756	360	820	340
Kaolin	390	180	436	155	420	220	518	304	454	230	762	404
Chalk fused	286	132	352	284	316	158	376	260	320	160	500	332
Magnesium carbonate	184	98	372	210	420	220	604	302	540	308	870	450
Lithopone	150	80	330	172	230	134	406	230	493	260	592	290
Ingredients	20 Volumes				30 Volumes				30 Volumes			
	Normal Condition		-40°		Normal Condition		-40°		Normal Condition		-40°	
	A	H	A	H	A	H	A	H	A	H	A	H
Carbon black	1010	571	1314	714	904	402	1010	515				
Zinc oxide	601	316	604	316	600	286	724	316				
Kaolin	436	226	820	438	442	242	780	450				
Chalk fused	322	200	500	329	276	186	470	326				
Magnesium carbonate	344	182	596	336	344	172	498	242				
Lithopone	421	230	556	348	588	880				

A = work expended in stretching.

H = work of elastic hysteresis.

The master mixture: normal condition -40°.

$$A = 120 \quad 184$$

$$H = 60 \quad 94$$

consider that according to the foregoing the loss of energy in elastic hysteresis is a function not only of the surface phenomena at the boundary of rubber-filler. A considerable part of the energy is expended in overcoming the frictional forces between the particles in the rubber mass. The increased viscosity of a frozen system increases considerably the frictional forces and disturbs the usual relations for all the ingredients studied. Originating in the process of stretching, the losses in elastic hysteresis vary inversely with the speed of stretching. At a high speed of stretching, heating of the rubber takes place. Applying to this case the second law of thermodynamics under the conditions of irreversibility of the process, we have $dQ < TdS$. The heat absorbed by the system is less than that which corresponds to the increase of entropy; hence it follows that in this case the entropy is created in the system itself, *i. e.*, it is increased. The increase of entropy is connected with the decrease of free energy, and therefore at rapid rates of stretching the hysteretic losses are smaller. Thermodynamics make it possible to relate the force of surface tension to the temperature T by a definite equation:

$$dU_s = -\sigma d_s + T \left(\frac{d\sigma}{dT} \right)_s dS$$

where d_s is the surface increment, and dS is the entropy increment. Consequently σ decreases with an increase of temperature, and the increment of surface energy (dU_s) is greater than the work performed on it (according to van-der-Waals $dU_s = 2.33 \sigma d_s$). This excess energy is obtained at the cost of the heat of the surrounding medium, and therefore under isothermal conditions the surface in the process of stretching is cooled. The mechanical work of rupture is substantially expended in the destruction of the surface film of the boundary of rubber-filler. On freezing rubber, there must be, according to the principle of Braun le Chatelier, a contraction of the surface, and on rupturing a frozen sample a greater consumption of mechanical energy. It is also evident that, for the optimum increase in tensile strength by true reinforcing agents, the decrease of film by freezing will be greater and the stretching of the rubber lower by considerable magnitudes. The free energy of the system is determined by the equation: $F = U - ST$, where F is free energy of the system, U is complete energy of the system, T is the absolute temperature, and S is the entropy. It can be readily seen that a decrease in temperature leads to an increase of free energy of the system. Hence, in freezing we should have on the one hand an increase of elastic hysteresis, and on the other hand a shift of the optimum increase in tensile strength for the given ingredient toward a smaller volume. The agreement between the experimental and theoretical data proves conclusively that the increases in tensile strength and in elastic hysteresis are conditioned by those surface processes which take place at the boundary of rubber and filler. The negative thermal coefficient of surface tension, obtained with the aid of the Helmholtz-Gibbs equation:

$$\sigma_f - U = T \frac{d_f}{dT}$$

equal to a few tenths of 1%, makes it possible to consider the system: rubber-filler, in the first approximation as a two-phase system. The absence of definite quantitative relations can be explained by the multi-phase condition of the system, the unknown components of which cannot be exactly determined.

Conclusions

1. The increase in tensile strength and the elastic hysteresis are undoubtedly conditioned by the surface processes at the boundary of rubber and filler. 2. On freezing, the optimum increase in tensile strength is shifted toward a smaller volume loading. 3. Because of the considerable increase of viscosity of the medium upon freezing, the forces of friction increase to such a degree that they mask the usual relations existing between A , R , and H for all ingredients.

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The Shock-Absorbing Quality of Rubber

L. Frumkin and V. Margaritov

The extensive use of rubber as a shock-absorbing and vibration-absorbing material makes necessary a definite criterion for this property of rubber. In his work on the problem of the shock-absorbing quality of rubber, Morrison¹ states: "To make possible an easy calculation of the rubber buffer, it is necessary to know: (1) the permissible working strain at the static loading for a given rubber, (2) the maximum strain permissible at the shock loading, and (3) the energy absorbed by a unit volume of rubber in the transition from static to shock loading." Reference to static load is made because, in this calculation, it is necessary to consider those static forces which act on the rubber before shock. The energy absorbed by the rubber in the transition from the static to the shock load is supposed by Morrison to be that energy which is absorbed by the rubber in its deformation by the shock. The question of the energy returned by the rubber in resuming its original form is not considered by him. Vetchinkin² in his study of the work of shock-absorbing aeroplane cords fails also to take into consideration the energy returned by the cord on resuming its original form, and bases his calculation only on the absorption by the rubber of a definite quantity of energy during stretching caused by the impact of the aeroplane against the ground. He mentions only casually that, by increasing the preliminary tautness of the cords, their hysteresis losses of energy are increased. However, such a concept of the work of a rubber shock-absorber seems to us inadequate. In fact, let us distinguish clearly between the work of shock-absorption of rubber and a steel spring. Of course it should be noted that for deformations by the highest possible stresses for rubber and for a steel spring, the former requires more energy per unit of weight. Thus, according to the above quoted paper by Morrison, 1 kg. of rubber absorbs 172 kg. of energy and 1 kg. of steel only 119 kg., *i. e.*, 44% less. According to Geer (cf. "The Reign of Rubber") the difference is many times greater, *viz.*, 10,000 kg. for rubber and 230 kg. for steel. However, the fundamental advantage of rubber over steel is that in the deformation of rubber there is considerable hysteresis loss of energy, and therefore the energy returned in resuming its original form is considerably smaller than the energy which caused deformation. This is connected with the ability of rubber to check vibrations. Morrison described the following simple test. When a strip of rubber 25 × 3 mm. is first stretched 30 per cent by a load of 2.7 kilograms, and then by hand for an additional 25 millimeters, and is suddenly released, vibrations continued at contractions and elongations for 12 seconds. A spring spiral of 12 millimeters' diam. and a wire gage 1.2 millimeters under similar conditions vibrated for 6 min. We believe that in the characterization of the shock-absorbing qualities of rubber, it is necessary to consider as an important factor this ability of rubber to arrest vibrations and to transform kinetic shock energy, *i. e.*, the energy of mechanical motion, into heat energy. Furthermore, the work of any shock-absorber, whether it is rubber, a spring, an oil, or a gas, consists of increasing the duration of the shock. The increased duration of the shock results in a correspondingly equal decrease of the force of shock. Evidently this shock-absorbing action is possible (as it actually is in practice) also where for instance the absorber nearly or entirely fails to transform

the mechanical energy into the heat energy. Thus we come to the conclusion that in the characterization of the shock-absorbing qualities of rubber, it is necessary to indicate in some way to what degree the rubber decreases the force of the shock.

The purpose of this work is: (1) to establish criteria for the evaluation of the shock-absorbing quality of rubber, corresponding to the ideas outlined above; (2) to develop a method of procedure for this evaluation; (3) to derive a relation between this quality of rubber and the nature of the fillers which it contains; (4) to investigate the changes in the shock-absorbing quality of rubber caused by repeated deformations, and (5) to examine experimental material with a view to explaining the physics of the deformation of rubber and the action of fillers.

I. Criterion for the Evaluation of the Shock-Absorbing Quality

If E is the energy expended in deforming rubber, and E_1 is the energy returned in the resumption of the original form of the rubber, then the magnitude of the relation $\frac{E - E_1}{E}$ shows what part of the deforming energy is transformed by the rubber into heat by one cycle of deformation and resumption of the original form. This relation, expressed in percentage, is called the shock-absorbing quality of the first degree, or the ability to check vibration:

$$W = \frac{E - E_1}{E} \times 100\%$$

Such a determination is, in the main, the application of Carnot's theorem to the theory of shocks.

Instead of a change in the quantity of energy a change in the quantity of motion might be considered; the result, which is numerically different from the value W , is related to it in a simple way, and therefore is not an independent value. As was shown above, in order to evaluate the shock-absorbing quality of rubber, the total duration of the deformation and the resumption of the original form of the rubber must be known, which may be denoted by τ . This may be assumed to be a criterion of the shock-absorbing quality of the second degree. To make evident the importance of this value τ , it must first of all be mentioned that, according to the theorem of the quantity of motion,

$$\int_0^t F dt = (mv)_1 - (mv)_2,$$

where F is the momentary value of the force of the shock, t the duration of the shock, and $(mv)_1$ and $(mv)_2$ the quantities of motion before and after the shock. However, according to the theorem of the mean value of the sub-integral function, the mean value \bar{F} of the acting force of the shock is equal to:

$$F = \frac{1}{t} \int_0^t F dt, \text{ or } \bar{F} = \frac{(mv)_1 - (mv)_2}{t}$$

Let us consider two cases of the shock, without the transformation of energy into heat and, for the sake of simplicity, with the striking body fixed, *i. e.*, the quantity of motion of the striking body changes the mark while retaining the absolute magnitude, and the complete change of the quantity of motion is equal to $2 mv$. Let it be assumed that in the first case the shock-absorber is absent, and that the shock is nearly instantaneous, lasting, at a rough estimate, for a period of time t equal to 0.001 sec. Then the mean force of the shock is equal to:

$$F_{0.001} = \frac{2mv}{t} = \frac{2mv}{0.001 \text{ sec.}}$$

If in the second case the shock-absorber is active, and the total duration of its deformation and resumption of the original form, denoted by τ , is equal to 0.1 sec., then the mean active force of the shock is equal to:

$$\bar{F}_{0.1} = \frac{2mv}{\tau} = \frac{2mv}{0.1}$$

Thus, in this example, the shock-absorber decreases the force of the shock 100 times. In general, this decrease becomes greater with increase in the time interval τ .

In summing up this part of the discussion, we come to the conclusion that the shock-absorbing quality of rubber is characterized by two magnitudes: W , which indicates the degree of transformation of mechanical energy into heat, and τ , which indicates to what degree the rubber decreases the force of the shock by increasing

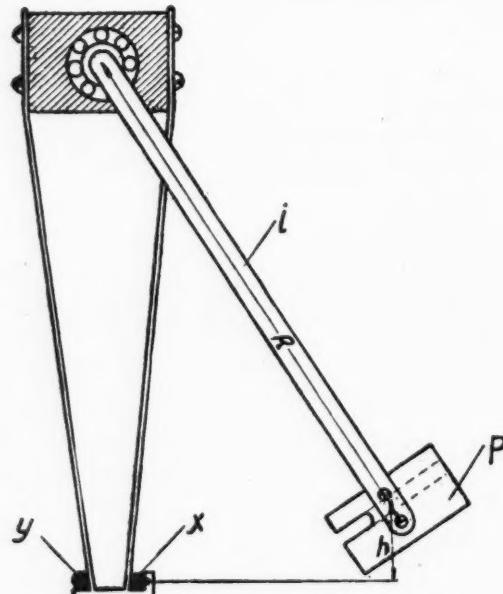


Figure 1

the elapsed time. These two magnitudes depend not only on the properties of the rubber, but also on the kinetic energy or the momentum of the shock. Even at a definite mv , every individual contributing factor is essential. In general, all the conditions of shock must always be taken into account, and in any comparison of the shock-absorbing qualities of various kinds of rubbers, all samples must be subjected to equal shocks.

II. Method of Determination of the Shock-Absorbing Quality

The problem was to subject rubber to shocks, and to be able at the same time to determine the kinetic energy before and after the shock, the quantity of motion before and after the shock, and the elapsed time of deformation and recovery of the original form of the rubber. It was also of interest to know the magnitude of

deformation. The experiments here considered are related to the deformations of stretching. The tests were carried out with the apparatus constructed by Chizhevskii. This consists of a pile-drive-like pendulum, shown schematically in Fig. 1, and by a reproduction from a photograph in Fig. 2. The pendulum consists of a sheet-iron arm i and a load P , and is suspended by means of two ball bearings. The weight P has a slot, extending through its entire length, with its depth reaching only up to the line of attachment. The extension of this slot, passing through the weight, is of less width. The ring samples of the rubber (inside diam. 16 mm., outside diam. 29 mm., thickness 2 mm.) are secured on the two steel rods x and y , which rest on shelves supported by a stationary vertical console. The shorter rod x (Fig. 2) is stationary and during the oscillations of the pendulum it passes through the slot of the load P . The longer rod y , resting on the other side of the frame, is caught by the weight of the pendulum in its oscillation from the right to left at the point of equilibrium and is returned to the former position on the backward swing of the pendulum. The distance between the axes of the rods on the shelves is 24 millimeters; their diameter is 3.5 mm. With these dimensions, the rubber before

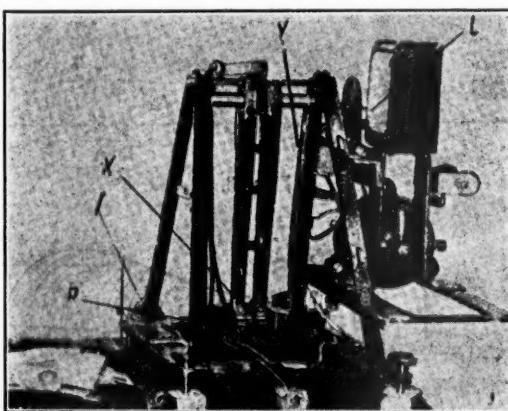


Figure 2

the action of the pendulum is practically unstretched while the ring itself assumes an elongated form and holds the rods on the shelves. The pendulum is so constructed that its center of gravity is on the line along which is situated the long rod when it is struck by the weight. The pendulum moves at an angle, with a reserve of the potential energy Ph (where P is the weight of the pendulum, equal in this case to 1 kilogram, and h the height of the altitude of its center of gravity), and when released strikes on its free swing forward at the long rod and stretches the rubber. The pendulum in its free forward swing passes through the position of equilibrium and has a kinetic energy equal to Ph . The energy of the pendulum is spent not only in its own ascent but also in stretching the rubber. It is obvious that the oscillation to the left (Fig. 1) will be considerably smaller than the initial swing to the right. In the swing of the pendulum from the left to the position of equilibrium, it is acted upon not only by the force of gravity, which depends upon the angle of displacement, but also by the force of the stretching, which depends upon the elasticity of the rubber. Without the rubber, the center of gravity of the slowly abating pendulum on its next swing toward the right would rise to the

altitude h . Actually it rises only to the lower height h_1 . The difference, $Ph - Ph_1$, is the difference of the kinetic energies, $E - E_1$, representing that quantity of energy which is not returned to the pendulum by the rubber, *i. e.*, the quantity of energy transformed into heat by the rubber. Thereafter the pendulum again stretches the rubber by the stroke, again swings backward, etc., whereby the amplitude of the oscillation gradually decreases. The oscillations are registered with a pencil on the evenly movable tape L (Fig. 2). The initial swing is actuated by hand, and was in all the tests equal to 90° , which corresponds to a reserve energy of 29.36 kg. per cm., since the distance R from the axis of suspension to the rod is 29.36 centimeters. As a result, curves of the decreased oscillations were obtained, which are given in Figs. 3 and 4 for two different kinds of rubber. It should be noted that these curves do not represent the normal curves of the abating oscillations, since, because of the great magnitude of the amplitudes and their changes, neither the period of oscillations nor the decrement of the abatement remain constant, and moreover these curves are asymmetrical.

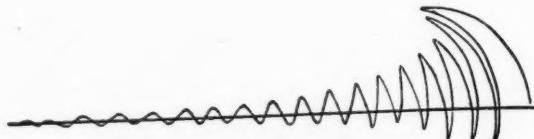


Figure 3



Figure 4

Now let us see how, with the use of these curves, the magnitudes that characterize the shock-absorbing qualities of rubber enumerated in the preceding section can be determined. The line described with the pencil by the declining pendulum represents the time axis, which is the abscissa axis. Then the ordinate of any point of the curve of abating oscillations is equal to the length of the perpendicular a (Fig. 4) dropped from the point of the pencil onto the line or onto the vertical plane in which lies the axis of the movable rod holding the sample. By multiplying the magnitude a by the constant M , which for the apparatus used is 10.81, and represents the relation R and the radius of the arc described by the pencil, we obtain the magnitude of the displacement of the center of gravity of the pendulum from the indicated vertical plane.

The Determination of the Magnitude W .—If A denotes the ordinate of a certain altitude of the registered curve (Fig. 4), an altitude corresponding to the free deflection of the pendulum, and h denotes the height of the ascent of the center of gravity at this ordinate A , then on the basis of elementary geometrical computation, the following connection between A and R can be established:

$$h(\text{cm.}) = R(\text{cm.}) - \sqrt{R^2 - M^2 A^2} (\text{cm.})$$

It is evident that the pendulum energy E , corresponding to a given amplitude of deflection, is determined by the magnitude of the product of its weight P and the height of the center of gravity h :

$$E = Ph = RP - P\sqrt{R^2 - M^2A^2} \text{ (kg./cm.)} \quad (a)$$

Since R and M are constant, we can determine for each ordinate A of the altitude of the curve of abating oscillation the kinetic energy returned by the rubber to the pendulum after the deformation, prior to the registration of this altitude, or, which is the same, the energy of the next shock. By taking the ordinates A_n and A_{n+1} of any two adjacent altitudes and calculating the corresponding E_n and E_{n+1} , we can easily determine the magnitude W corresponding to those conditions when the energy of the shock is equal to E_n :

$$W = \frac{E_n - E_{n+1}}{E_n} \times 100\%$$

In practice this can be easily carried out in the following manner. Once for all a nomogram is developed for the apparatus used, expressing according to formula (a) the energy E_n through A_n (Fig. 5). With the aid of this nomogram and on the basis of the registered curves, graphs are constructed to show the relations of the energy of the pendulum at the end of the first, second, third, and other periods

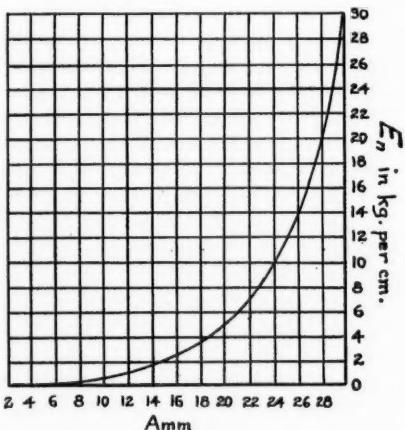


Figure 5

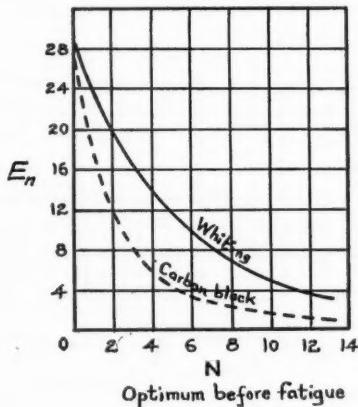


Figure 6

to the ordinal number of this period in the course of the process of vibration abatement. Zero on the axis of abscissa corresponds to the beginning of the first period, *i. e.*, to the initial deflection of the pendulum at a right angle. From these curves $E = f(n)$, examples of which for the rubbers containing carbon black and whiting are given in Fig. 6, the value W is easily calculated for any given value E_n . By way of example, let us examine such a calculation of W in Fig. 6. The energy of 12 kg. per cm. corresponds for the carbon black mixture to the second deflection, 12 kg. per cm., and is E_n ; in the next deflection $E_{n+1} = 8$ kg. per cm. Consequently

$$\frac{E_n - E_{n+1}}{E_n} \times 100\% = W = 33\%$$

Hence, at a shock with energy of 12 kg. per cm., the rubber absorbs 33 per cent of the shock energy. To show in what way the shock-absorbing quality W depends upon the shock energy, graphs were developed, an example of which is given in Fig. 7. Since in the stretching and contraction of rubber, the absorbed mechanical

energy is transformed into heat, the heat effect of the deformation of rubber was determined in addition to the measurement of the absorbed mechanical energy. However, the measurement of the heat effect, carried out with a thermocouple sewed into the ring samples and connected with a galvanometer during stretching, gave no results of value, no well marked relation between the heating of the sample and its shock-absorbing quality being found. The reason for this was that, under the conditions, every sample, regardless of its shock-absorbing quality, transformed into heat during the entire time of the decreasing oscillation the same quantity of mechanical energy, which is equal to the reserve of energy of the pendulum at its initial deflection.

Therefore the individual ring samples differed only in the duration of the decreasing oscillations which produced an equal calorific effect. The differences in the temperature effects are governed only by the fact that, at the higher rate of heat formation, heat is transmitted to the surrounding environment to a much less degree. To obtain more characteristic results, the samples must be subjected to an equal degree of identical deformations. Under these conditions the differences in the thermal effects are determined first of all by the part of the deforming energy transmitted into heat by the sample.

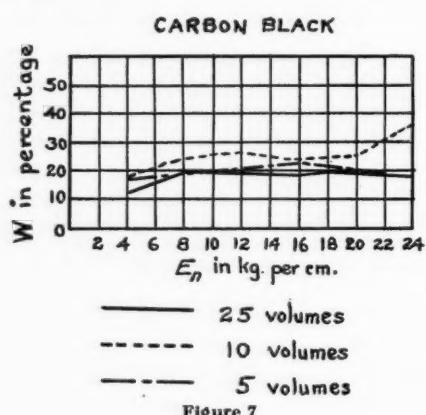


Figure 7

thermocouple. Thus the temperature of a thermocouple was determined with a precision of 0.025° . After deformation of the sample began, the galvanometer reading increased, corresponding to a thermal equilibrium between the temperature of the sample heated by the deformation and the surrounding medium. In addition to the determination of the increase of temperature, the time elapsed during the increase was measured. To compare the thermal effect of the deformation of rubber with its shock-absorbing quality, a determination of the calorific effect and not of the temperature would be a better procedure. However, the difficulties of an accurate determination of the conduction of heat and the surface loss of heat, requiring a number of computations, with errors affecting the results, compelled the use of the latter procedure.

Determination of the Quantity of Motion.—In this machine the rubber returned the absorbed quantity of motion to the same body (the pendulum weight) which had previously deformed the rubber by shock. Consequently, to determine the quantities of motions and their changes, it is sufficient to know the mass of this weight (this in technical units is equal to $1/9.81$ kg. per sec.) and its velocity at the moment

These tests were carried out in the following manner. Thermocouples (copper-constantan wire of 0.1 mm. diam.) were sewed into the inner core of the rubber strips cut from the same batches used in preparing the ring samples. These strips were fastened in the clamps of a Schopper fatigue machine, and were stretched to 275 per cent for 100 times in 1 min. The electric current was measured with a mirror galvanometer with a sensitivity of 2.6×10^{-9} amp. on a 1 mm. scale at a distance of 1 meter. The heating of the thermocouple by 1° caused a displacement of 35–40 mm. on the scale in the field of vision, depending on the

of shock and at the moment of the separation from the rubber contracted after deforming. This velocity is related to the height of the elevated center of gravity h by the simple equation $V = \sqrt{2gh}$. Replacing the value (a) for h by the value of the ordinates of altitudes A measured from the curves of abated oscillation, there results:

$$V = \sqrt{2g} \times \sqrt{R - \sqrt{R^2 - M^2 A^2}}$$

If a large number of determinations of the values mv and V is required, it is convenient as before to use a nomogram, which in this case is nearly rectangular.

Determination of the Elapsed Time of Deformation and Recovery.—Since the abscissae of the registered curves of the type in Fig. 4 represent time, it follows that every segment represents a certain interval of time. At a ribbon speed of 90 cm. per sec., the ribbon is displaced 1 centimeter in 0.66 second. In Fig. 4 the point e

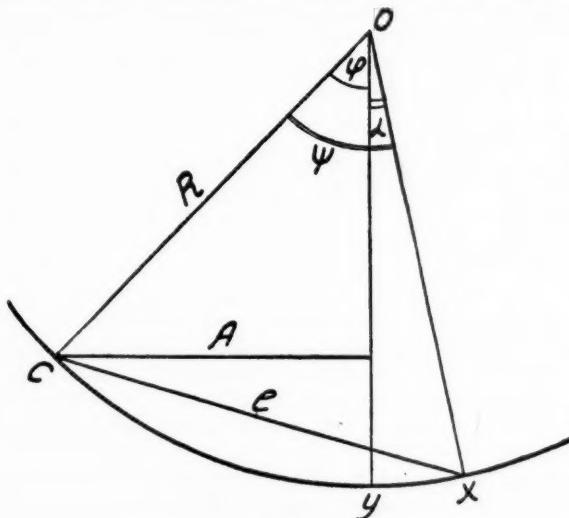


Figure 8

indicates the moment of initial deformation upon stretching the rubber, and the point f the moment of the termination of recovery after this deformation. Multiplying the length of the segment ef , expressed in centimeters, by 0.66 second, gives in seconds the elapsed time of deformation and recovery. Having determined the energy and motion, corresponding to A and h , the shock-absorbing quality of the second degree can be compared with the conditions of the shock.

Determination of the Magnitude of the Stretching of Rubber.—Fig. 8 shows that the height of the ordinate A_1 (Fig. 4) measured from the registered curves, and corresponding to some calculated deflection of the pendulum retarded by the rubber, is related to the length l of the extended and folded double ring by the formula:

$$l = 2R \sin \frac{1}{2} \left[\arcsin \frac{MA_1}{R} + \alpha \right]$$

Here R and M have the previous denotations, α is the center angle determined by the arc of the radius of 28.5 mm. length equal to the sum of the double radius of the rods and the distance between their axes; this length is equal to one-half of the

original length of the ring before stretching; the angle α is 4.8° . To express the elongation of the rubber in percentage, it is necessary to calculate the magnitude:

$$\frac{l - l_0}{l} \times 100\%$$

Here again it is convenient to use a nomogram connecting the relative elongation with the magnitude A measured from the curves. The present paper shows that all the values required for the determination of the shock-absorbing quality of rubber are expressed by the simple functions represented by the ordinates A and A_1 measured directly on the curves registered by the apparatus. The apparatus here described was intended for studying the shock-absorbing quality of rubber on stretching and prior to application of a shock load. However, by replacing the stationary rod holding the sample, this apparatus can also be used for measuring the work of a preliminary stretching. In the program of our laboratory, an investigation by the pendulum method of the shock-absorbing quality of the rubber not only in the process of stretching but also in the process of contraction, bending, and transmitting of the shock through the depth of the rubber, was included.

III. The Shock-Absorbing Quality of Rubber under the Initial Conditions

In the following section, it is shown that the shock-absorbing quality of rubber is considerably changed after the rubber has been subjected to repeated deformations. Furthermore, it was observed that a long rest (24 to 48 hours) of the rubber after repeated deformations caused new changes in the shock-absorbing quality, without a return to the original values. By the initial state of rubber is meant its condition for a considerable length of time (not less than 24 hours) after vulcanization but prior to deformation. It is obvious that these conditions are not normal for rubber which has undergone or is undergoing work, but the data on the shock-absorbing qualities obtained under these conditions are valuable, first for comparing the results of other mechanical properties of the rubber determined in the usual way under these initial conditions, and secondly for explaining the changes in the rubber caused by deformations.

To determine the action of individual ingredients on the shock-absorbing qualities of rubber, a master mixture of the following composition was used:

Smoked sheet	100
Sulfur	3
Zinc oxide	5
Stearic acid	0.5
Mercaptobenzothiazole	0.6
Tetramethylthiuram disulfide	0.06

to which was added each of the following fillers in proportions of 2.5, 5, 10, 15, 20, and 30 parts per 100 parts by volume of rubber: carbon black (GET), zinc oxide, magnesium carbonate, kaolin (Turbov), whiting, lithopone, and barytes. Vulcanization in all cases was at an optimum for each mixture. The experiments were carried out with two parallel samples, which as a rule gave good checks. In case of disagreement in the results, the tests were repeated with a greater number of samples. To avoid a cumbersome quantity of data, the results for only four of the more characteristic ingredients, *viz.*, carbon black, zinc oxide, kaolin, and whiting are given.

1. *Dependence of the Shock-Absorbing Quality W on the Energy of Shock.*—This relation is shown in Figs. 7, 9, 10, and 11. These graphs show that with increase in the energy of shock above 10 to 20 kg. per cm., the magnitude W , *i. e.*, the ability

of the rubber to transform the mechanical energy into heat, is unchanged for the master mixture, is more or less constant for the kaolin mixture, is somewhat less for the zinc oxide, and is greater for the whiting and carbon black mixtures.

2. *Dependence of the Shock-Absorbing Quality τ on the Energy of Deformation.*—This relation is shown in Fig. 14 only for the sample containing 20 volumes of carbon black. With the other mixtures, an analogous trend of this dependence was observed, with variations only in the absolute values of τ , corresponding to some definite deforming energy. A comparison of the absolute values was made at $E_n = 12$ kg. per cm., and this is shown graphically in Figs. 12 and 13. Figure 14 shows

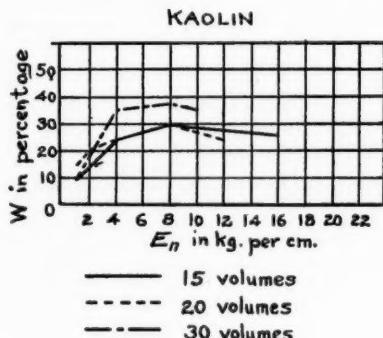


Figure 9

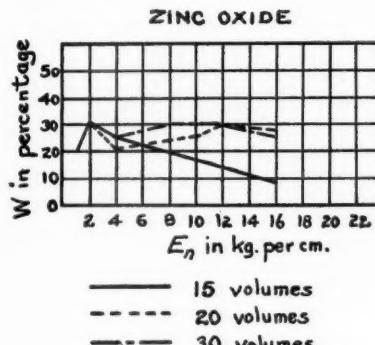


Figure 10

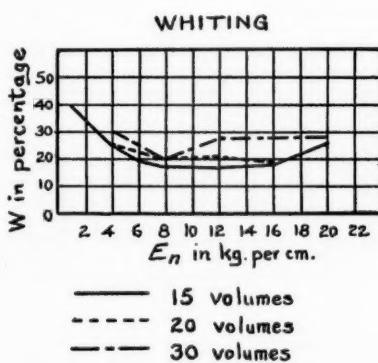


Figure 11

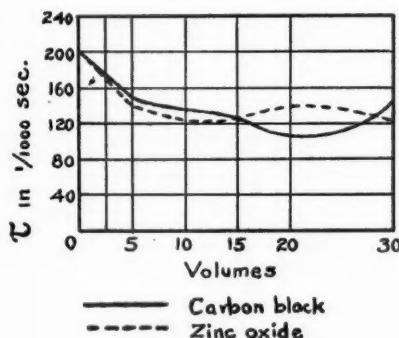


Figure 12

that, at a small energy of shock, the shock-absorbing quality τ is greater. This means, for instance, that in absorbing a shock with one-half the energy, the rubber buffers the shock with a mean force 4 to 5 times smaller.

3. *Dependence of W on the Degree of Rubber Filling.*—The value of W for the different rubber mixtures was compared for deformations of the same shock energy of 12 kg. per cm. The results are shown in Figs. 15, 16, 17, and 18.

Of considerable interest is a comparison of these curves with other characteristics of the rubber, *viz.*, its hysteresis and elasticity as functions of the degree of loading. However, the data on hysteresis should in this case be expressed not in the manner commonly used in the literature as the difference of the energy expended in def-

formation and returned in the recovery by the rubber. Here, since E_n and E_{n+1} represent the energies of stretching and contraction, and are measured at rapid deformations, it is necessary, according to the equation:

$$W = \frac{E_n - E_{n+1}}{E_n} \times 100\%$$

to determine the hysteresis from the ratio of the difference of energy to the energy of deformation. Since the hysteresis of rubber depends also upon the nature of the

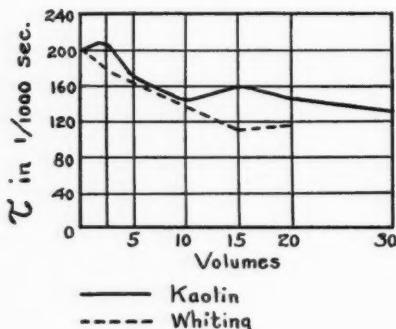


Figure 13

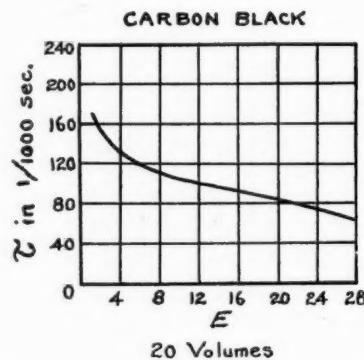


Figure 14

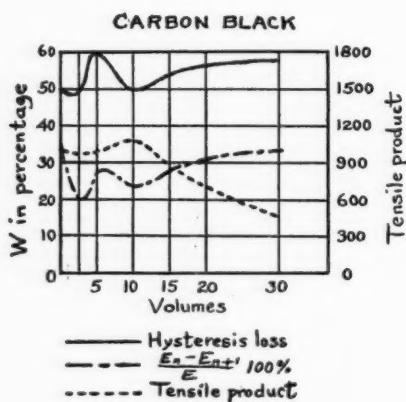


Figure 15

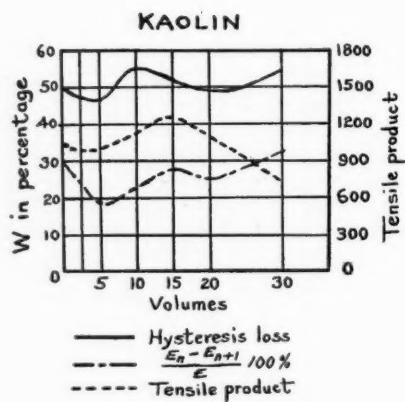


Figure 16

ingredient in the rubber, the present results were compared with the published data on hysteresis previously obtained with the same fillers.³ Figures 15 to 18 show that the curves of the relation between W and between the hysteresis and the filler, and calculated by the method shown, are identical. The differences in the absolute magnitudes of the energy must be explained by the great difference in the velocities of deformation at which such data were obtained. In comparison with other data on hysteresis, the similarity of the curves appears less sharply defined.⁴ A comparison with the curve of the ratio of the tensile product to the filler, constructed on the

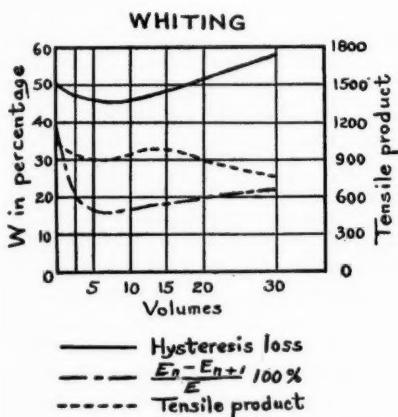


Figure 17

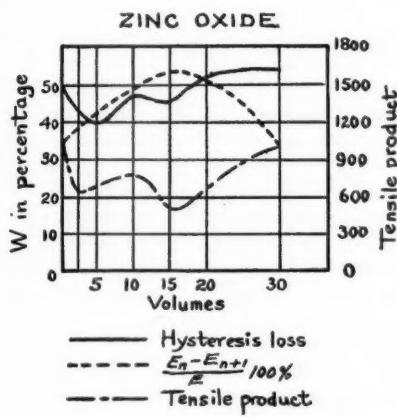


Figure 18

basis of the data given in the same work,³ shows that for true reenforcing agents, such as carbon black and zinc oxide, the second minimum of the curve W corresponds to the maximum tensile product; for kaolin the minimum W is shifted toward the greater proportion of filler, while whiting gives no second minimum, and a well defined relation between the curves W and the tensile product was not evident.

4. The Relation between W and the Thermal Effect of Repeated Deformations.

—A comparison of these two values shows that, generally speaking, an increase in the one is accompanied by an increase in the other. The mixtures with zinc oxide are exceptions, which have high W values at a comparatively small temperature effect. This may be explained by the relatively high heat conductivity of zinc oxide. To illustrate the relation between W and the thermal effect, Fig. 19 gives the data for only the largest volumes of loading (30 volumes), where this relation is most clearly evident.

5. The Dependence of Shock-Absorbing Quality τ on the Filling.—This relation is shown in Figs. 12 and 13. As a rule, a pure mixture gives the greatest τ value. With an increase in the filler content, it at first decreases and then increases, the only exception being the mixture with 2.5 volumes of kaolin. Of interest is the observation that the τ values for two rubber mixtures containing ingredients of distinctly different nature (whiting and carbon black) differ but very little.

IV. Changes in the Shock-Absorbing Quality of Rubber under Fatigue and at Rest

1. The Method of Measurement.—The fatigue tests of the ring samples were made on a Schopper fatigue apparatus shown in Fig. 20. The machine was set at a

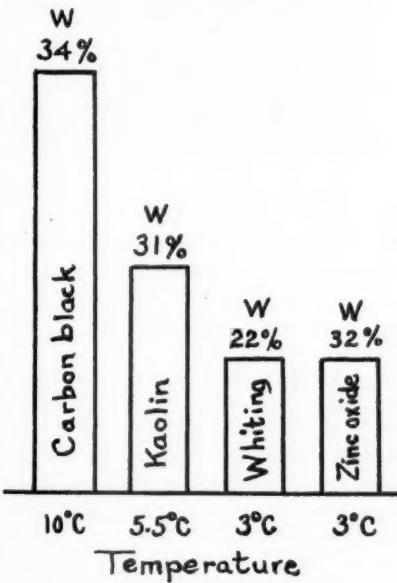


Figure 19

speed of stretching and contraction of 100 cycles per min. The maximum elongation at each stretching was equal to 275 per cent of the original length of the ring sample. The shock-absorbing quality of the samples was measured on the pendulum apparatus, described in Section II, under the following conditions. (1) At the initial state of the sample, *i. e.*, before the rubber had been deformed. (2) After 10 cycles of stretching and contraction on the Schopper machine. This latter time was of interest because, as is known, during the first cycles of stretching there is a change in the area of the hysteresis loop, which ceases toward the seventh to ninth cycle. Evidently the shock-absorbing quality, which is related, as was shown in Section III, to the magnitude of the elastic hysteretic loss, must also change with the first ten cycles. (3) After 500 cycles of deformation; the measurements were made 15 to 20 min. after the samples were removed from the machine to cool to room temperature. (4) After the sample had rested for 2, 4, 8, 24, and 48 hours. (5) After renewed fatigue of samples rested after 500 cycles. (6) After the second period of rest of 2, 4, 8, 24, and 48 hours. (7) After a fatigue of 1000 cycles for some of the samples instead of the 500 cycle as in (8). After a rest for 2, 4, 8, 24, and 48 hours of samples of 1000 cycles. Thus the measurements made with one set of samples are indicated under (1) and (5) and with the other parallel samples under (1), (2), (6), and (7). All the measurements of the shock-absorbing quality are

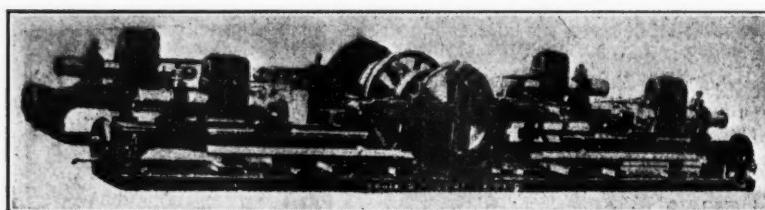


Figure 20

shown in graphs for the carbon-black samples in Figs. 21, 22, and 29, for the zinc-oxide samples in Figs. 23, 24, and 30, for the kaolin samples in Figs. 25, 26, and 31, and for the whiting samples in Figs. 27, 28, and 32. The graphs form broken lines, and no conclusions with respect to the intermediate states of the rubbers could be drawn.

2. The Results of the Tests.—In surveying the results of the experiments, it is necessary to consider that the changes in the shock-absorbing quality W during a certain period of the history of the sample, though small by difference, may be considerable when expressed in percentage of the original magnitude of W . For example, the shock-absorbing quality of a mixture containing ten volumes of carbon black decreases after the first ten cycles from 24 to 18 per cent or by a difference of 6 per cent (Fig. 21). This decrease in the ratio to the original magnitude of W is equal to 25 per cent. The graphs show that the shock-absorbing quality of most of the samples is considerably decreased in the first ten cycles of fatigue. This is particularly clear with all the samples containing carbon black in all proportions and with samples containing little zinc oxide. In the samples with 10 to 30 volumes of whiting and large proportions of zinc oxide (30 volumes), there was on the contrary a considerable increase of W for the initial 10 cycles of fatigue. In the concluding part of this paper, an attempt will be made to explain the increase of the shock-absorbing quality of these rubbers by the initial cycles of fatigue. A survey of the results of the first 500-cycle fatigue discloses a further considerable de-

crease in the magnitude W for the carbon-black and zinc-oxide samples, while for those with large volumes of whiting (20 to 30) a small rise of the curve is evident. It is interesting that W for the kaolin mixtures is changed quite considerably in the initial ten cycles of fatigue and then remains unchanged during further fatigue. It has already been mentioned that the fatigued samples were allowed to rest. The change in W was followed during this period of rest. The following segment of the curves gives these characteristics. We observe here a series of highly interesting and entirely new but fully explicable conditions. In the carbon-black samples the magnitude W continues to decrease during the first 2 to 4 hours of rest. The duration and the degree of this decrease depends on the volume of filler. The exception is a mixture with 15 volumes of carbon black (optimum increase of strength), where the recovery of the shock-absorbing quality takes place at once. In the rubber containing zinc oxide, the conditions are approximately the same, except that the period of decrease of W is shorter. Similarly to the carbon-black sample, the samples loaded with filler to the optimum increase of strength show a more rapid recovery of the shock-absorbing quality. Kaolin acts similarly to the mixtures with true reinforcing agents, but is somewhat weaker. An increase in

CARBON BLACK

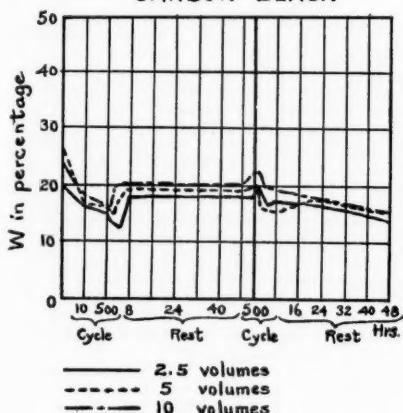


Figure 21

CARBON BLACK

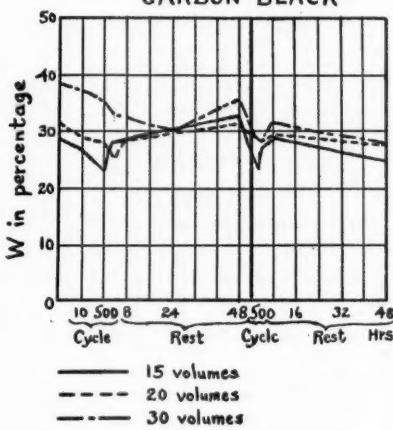


Figure 22

the volume of whiting results in a more rapid recovery of the shock-absorbing quality during rest, but this effect is not clearly demonstrated. A more prolonged rest (48 hours in the experiments) leads to a more or less complete recovery of the shock-absorbing quality, depending on the nature of the filler. The exceptions are rubbers heavily loaded with whiting, which show a decrease of the shock-absorbing quality after an improvement at the beginning of rest. After a rest of 48 hours, the samples were again subjected to fatigue of 500 cycles under the conditions previously described. The action of the additional fatigue and rest is shown in the graphs of the second right half of the diagrams. As might be expected, the repeated fatigue caused another sharp change in the shock-absorbing quality. The samples containing but little carbon black (2.5 to 10 volumes) showed an increase in their shock-absorbing quality instead of a decrease produced in the first stage of the fatigue. After a rest there was an increase in the shock-absorbing quality at the beginning, followed by a decrease. Thus, the trend of the change in the shock-absorbing quality was to some extent contrary to that of these changes during the first stage of fatigue and the following rest at the initial period.

For the samples containing considerable carbon black (15 to 30 volumes) the course of the curve is analogous to the first one, but its character is more sharply pronounced. The samples with zinc oxide produced results analogous to those of the carbon-black samples, and thus this type of curve may be regarded as typical of the true reënforcing agents. The following conditions must be noted. The

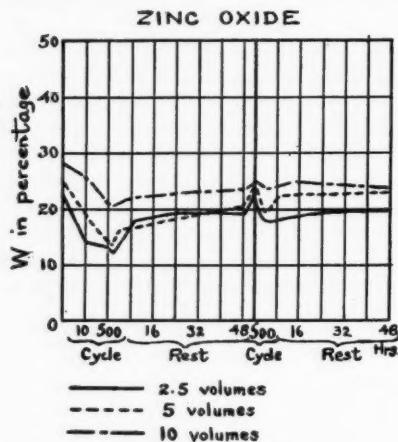


Figure 23

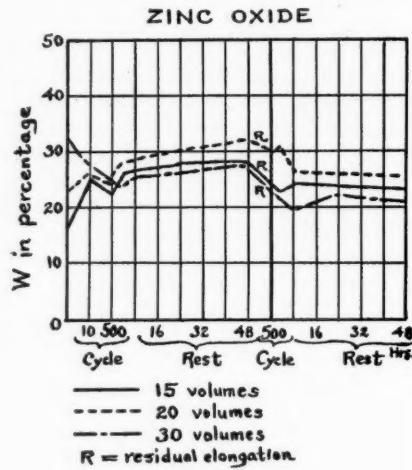


Figure 24

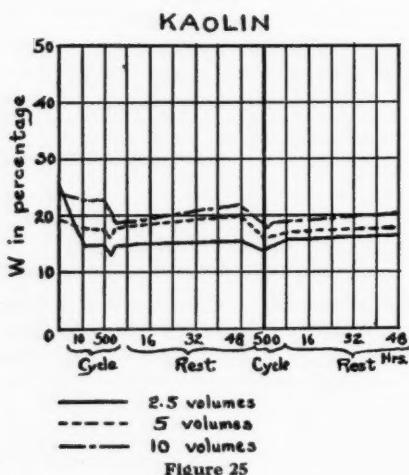


Figure 25

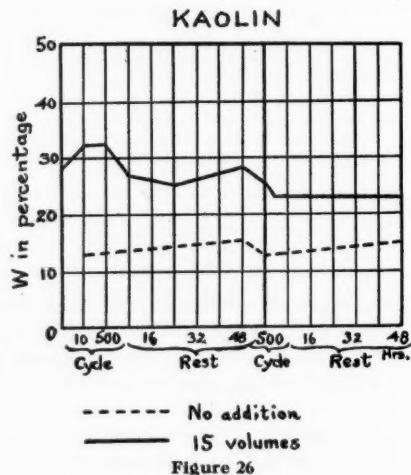


Figure 26

samples heavily loaded with zinc oxide (15, 20, and 30 volumes), whiting (30 volumes), and kaolin (20 to 30 volumes) showed such a great residual deformation immediately after the second fatigue and even after the first two hours of rest that measurements of the shock-absorbing quality were difficult. These stages of the history of the sample, for which no determinations of the shock-absorbing quality were made, are denoted on the graphs by the letter *R*.

For the same reason any conclusions with respect to the kaolin mixtures must be confined to the samples with small loadings. Here the picture of the first fatigues

is fully repeated, but is expressed less clearly. The whiting samples did not give any typical picture, though some regularity was observed. It is of interest to note that all rubbers, depending on the nature of a filler, decrease more or less in their shock-absorbing quality as the result of prolonged rest (48 hours) *after the second fatigue*. The graph of the change of the shock-absorbing quality W of the master mixture after fatigue and rest is shown in Fig. 26, which shows that all the changes of W are here considerably smaller. A long rest (48 hours) after the second fatigue increases somewhat the shock-absorbing quality. The second fatigue produces a comparatively great decrease of the magnitude W , but the character of the recovery which follows corresponds fully with the picture obtained after the first rest. The curves, given in Figs. 21 to 28, show the changes of the shock-absorbing quality as the result of the double 500-cycle (or a total of 1000 cycles) fatigue of rubber, with an intermediate rest. To make clear the influence of the rest between the two fatigues on the shock-absorbing quality of the rubber, parallel tests of the samples after a continuous 1000-cycle fatigue were carried out. The results of the tests for

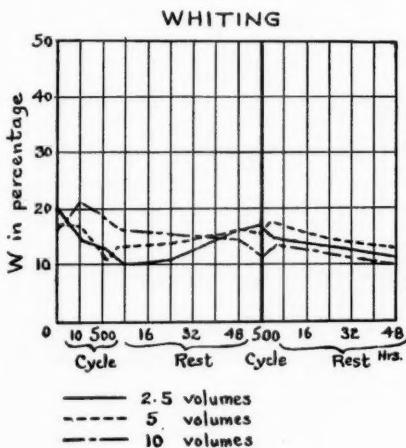


Figure 27

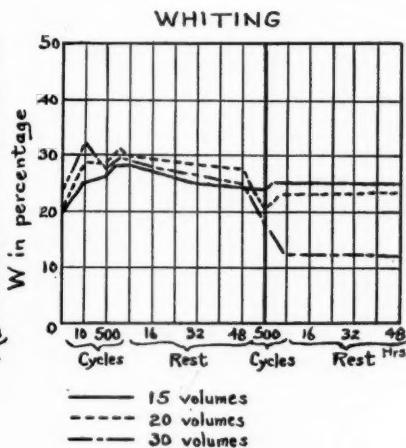


Figure 28

optimum loads of the fillers are shown in Figs. 29 to 32. To make convenient a comparison of the action of the continuous (1000 cycles) and the two-stage (500 + 500 cycles) fatigue, the graphs are arranged in the following manner. The first point of the graph for the continuously fatigued rubber, which characterizes the shock-absorbing quality measured immediately after the fatigue, has the same abscissa as the point corresponding to the end of the second 500-cycle fatigue for the parallel sample. Here, too, interesting relations are observed. The curves for the carbon-black samples in the first 4-hour rest are concordant; in the following period of rest the curve for the continuous 1000 cycles is lower, but the character of the curve remains the same. In case of the zinc-oxide samples, the recovery of the shock-absorbing quality begins directly after the continuous 1000-cycle fatigue, yet the curve is situated below the curve showing the conditions of rest of the rubber which was subjected to the two-stage 500-cycle fatigue. The curves for the kaolin mixtures are nearly concordant, though the curve representing the rest after a continuous fatigue is somewhat lower. The whiting mixture, as in all previous cases, does not give a sufficiently clear picture, but it is analogous to the

mixtures with other fillers; its curve of rest after a continuous fatigue is lower. It is possible to conclude that continuous fatigue causes a sharper decrease of the shock-absorbing quality of the rubber than the corresponding number of cycles of fatigue by stages with an intermediate rest.

The differences in the shock-absorbing quality of the rubbers described in Section III, which vary with the nature of the fillers, show that the magnitude W is a sensitive criterion of the ability of rubber to transform mechanical energy into heat. By determining other magnitudes by the method described in Section II, and calculating the results from the measurements on the curves registered by the pendulum apparatus, extensive data on the elastic properties of any rubber mixture at a dynamic load can be obtained. Figures 15 to 18 show that the evaluation of the optimum mechanical properties of a rubber mixture on the basis of such a criterion, as is commonly done in factory practice in terms of tensile product, does not foretell the best performance of the rubber under a dynamic load. We can speak of different optimum increases in strengths, depending upon whether we are inter-

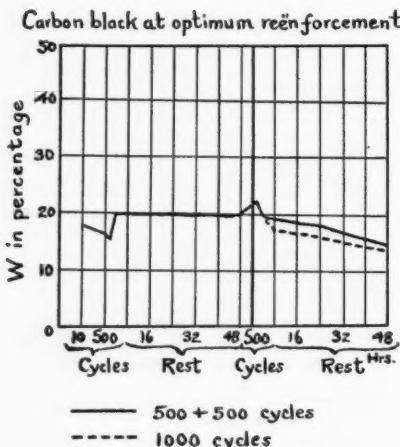


Figure 29

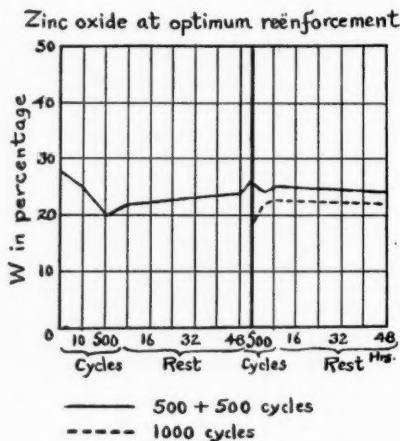


Figure 30

ested in the best performance of the rubber at a slow elongation or under the actual working conditions of shock-absorption. Furthermore, the rather considerable changes in the shock-absorbing quality of rubber produced by repeated deformation, which differ in various cases not only in their relative magnitude but also in their direction, make doubtful the value of the results of conventional methods of testing samples which have not been previously subjected to repeated deformations. The results of these tests do not make possible an estimation of the performance of the rubber under practical conditions where there is severe deformation. We consider that in addition to the development of a dynamic method of testing of rubber, it is desirable to make a systematic study of the changes in elastic characteristics, which are caused at some stage of the history of the sample, such as more or less repeated deformation, rest, etc. In the changes in the shock-absorbing quality of rubber produced by fatigue, the features which are surprising are: (1) the considerable magnitude of these changes; (2) the difference in their direction with active and inert fillers, and (3) the continuation of these changes during the initial period of rest in the same direction as during the fatigue, or the inertia

of fatigue, if the process may be thus designated. The facts enumerated here show again the complexity of the processes which take place in the deformation of rubber, not only in the rubber-filler system but also in the pure vulcanizate-filler system. In an effort to find at least a partial explanation of these facts, certain concepts of the changes of rubber during fatigue must be accepted.

The preliminary results of the investigations of the Physical Laboratory of the Scientific Research Institute of the Rubber Industry tend to confirm partially our views, though they require considerable correction and development. The theory originating from the present work may be thus stated. An active filler in rubber is more or less fully wetted by the pure vulcanizate, *i. e.*, the two are mutually bound. This wetting, which takes place in the formation of the uncured mixture, is also retained in the vulcanizate. In the process of repeated stretching of the rubber, the mutual displacements of the pure vulcanizate and the filler particles cause some disruption of the cohesion between them. This results in a weakening of the rubber and a resulting decrease in the shock-absorbing quality. With an

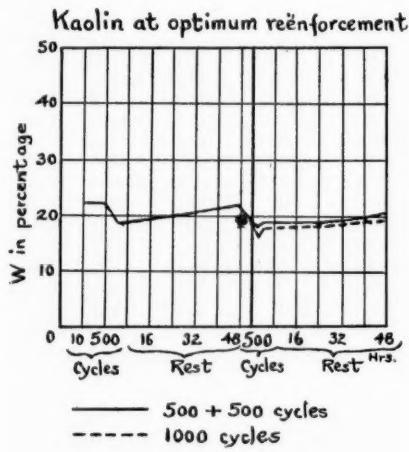


Figure 31

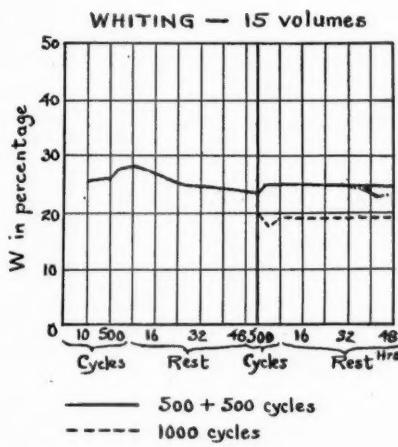


Figure 32

inactive filler, however, the wetting of the filler by the rubber and the pure vulcanizate is insignificant, *i. e.*, there is practically no bonding. The repeated stretching and the now considerable mutual displacements result in an improvement of the wetting and a more intimate occlusion of the filler. This results in a reenforcement of the rubber and an improvement in its shock-absorbing quality. With further excessive repeated stretching, a weakening of the rubber may be expected. Proceeding from this hypothesis, it might be expected that the increase in the shock-absorbing quality would be accompanied by an increase in the density of the rubber, because of the disappearance of the minute interstices between the particles of the filler and the vulcanizate. This usually leads to an increase of the specific gravity. Conversely, a decrease in the shock-absorbing quality should result in a lower density. Accordingly the densities of 23 samples before and after a 500-cycle fatigue and during a rest period of 24 hours were determined. It was expected that the tests would show changes in the density to an extent corresponding to the changes in the shock-absorbing quality. The table here given shows entirely different results. As is evident, in all cases except those of maximum filling with

kaolin and whiting, the fatigue caused an increase of the specific gravity of the rubber. The master mixture, which was almost a "pure rubber" mixture, showed one of the greatest increases in density. The latter phenomenon would indicate that the changes in density may be ascribed solely to certain processes in the pure vulcanizate. However, the differences in the changes of the density of the rubbers compounded with equal volumes of various fillers shows that the processes at the boundary surface here play an important part. During the first 2 to 8 hours of subsequent rest, the density returned nearly to its original value.

CHANGES IN DENSITIES OF THE RUBBERS AT FATIGUE AND REST

Names Fillers	Volume of Filler	500-Cycle Fatigue				After a Rest of			
		Before	After	2 Hrs.	4 Hrs.	8 Hrs.	24 Hrs.	48 Hrs.	
Carbon black	2.5	0.978	0.989	0.984	0.983	0.984	0.984	0.984	
	5	1.009	1.018	1.018	1.009	1.009	1.009	1.009	
	10	1.038	1.047	1.037	1.037	1.037	1.037	1.037	
	15	1.068	1.079	1.067	1.067	1.067	1.078	1.068	
	20	1.084	1.096	1.083	1.083	1.083	1.084	1.083	
Zinc oxide	2.5	1.056	1.071	1.071	1.056	1.056	1.056	1.056	
	5	1.164	1.176	1.163	1.163	1.163	1.163	1.163	
	10	1.336	1.347	1.333	1.333	1.333	1.334	1.336	
	15	1.511	1.520	1.505	1.510	1.510	1.510	1.510	
	20	1.591	1.620	1.620	1.605	1.600	1.600	1.600	
Kaolin	30	1.627	1.647	1.627	1.627	1.627	1.627	1.627	
	2.5	1.012	1.024	1.012	1.010	1.010	1.012	1.012	
	5	1.028	1.041	1.035	1.028	1.029	1.028	1.028	
	10	1.091	1.102	1.090	1.090	1.090	1.090	1.090	
Whiting	15	1.150	1.172	1.144	1.144	1.133	1.160	1.160	
	2.5	0.992	1.014	1.010	1.000	1.000	1.000	1.000	
	5	1.030	1.051	1.040	1.040	1.030	1.030	1.029	
	10	1.112	1.126	1.116	1.112	1.112	1.112	1.112	
	15	1.156	1.170	1.159	1.158	1.159	1.159	1.159	
Master mixture	20	1.181	1.203	1.201	1.202	1.208	1.208	1.205	
	30	1.313	1.298	1.298	1.300	1.300	1.313	1.310	
	..	0.959	0.978	0.969	0.969	0.969	0.969	0.969	

All measurements are at 16° to 18°. The probable error of a separate result does not exceed 0.002.

However, in some cases the recovered density was lower than the original, but it gradually increased and attained the full value. The experiments with the kaolin and whiting mixtures, which gave entirely different results, were repeated, as a result of which consistently uniform results within the limits of the experimental errors were obtained. In this way it was possible to establish the hitherto unexplained fact that there is a change of density of the rubber in the process of work and rest, and that it is in some way connected with the presence of certain fillers. There is no explanation for the inertia of fatigue which was observed during the time of rest. It may only be noted that, as can be seen in Fig. 29, this inertia with the carbon-black mixtures was considerably greater after a long continuous fatigue than after a short fatigue. The shock-absorbing quality of the second degree, *i. e.*, the capacity to increase the duration of the shock and thereby to mollify it, which is characterized by the elapsed time τ of deformation and recovery, proved to be, as can be seen in Figs. 12 and 13, almost independent of the nature of the filler. The dependence upon the energy of the absorbed shock, shown for the carbon-black rubber in Fig. 14, proved again to be nearly the same for all the rubber mixtures investigated. This condition, as well as the fact that the greatest τ is produced by the master mixture (Figs. 12 and 13), shows that the shock-absorbing quality of the second degree is conditioned by the properties of the pure vulcanizate and is almost independent of the properties of the fillers.

Acknowledgment

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- ² Vetchinkin, "Dinamika Samoleta," **1933**, 197-206.
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The Determination of the Optimum Vulcanization by Means of the Residual Elongation

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As is well known, various methods have been proposed for determining the optimum vulcanization of rubber. These methods depend either upon physico-chemical examination or upon mechanical tests. In routine control the mechanical method of determination is used for the most part, because it requires but little time, and in addition this method has the advantage of showing directly by mechanical tests whether the vulcanizate being tested passes the requirements or not. The results obtained by this method frequently do not agree with those obtained by other methods. Of the many common methods of testing, determinations of the tensile strength and of the ultimate and residual elongation are the methods most frequently used. These three properties are measured simultaneously by one determination with the apparatus in most widespread use, *i. e.*, the Schopper and the Scott machines. In special cases the resistance to abrasion, bending strength, hardness, and other properties are determined in addition. Considerably less often the hysteresis and Young's modulus of elasticity are determined. All these determinations are of significance in only a limited way, for the conditions under which the tests are carried out in the laboratory are not comparable to the actual service of the products. For basic reasons, this fundamental shortcoming cannot be avoided in the laboratory, though a few of the measurements do approach the true properties found in service. Of course, the results obtained in the laboratory are greatly influenced and made less reliable by other secondary factors, among which are the phenomenon of aging under natural conditions, prolonged stressing, etc.

All mechanical tests are subject to still another error which detracts to a large extent from their value, namely, that none of the methods mentioned above indicates the change which takes place during the determination itself. The Young modulus alone does not have this drawback. As a matter of fact, the residual elongation should indicate the change which is actually taking place, though it is known that even this property cannot be shown to be a simple function of the time of vulcanization.

The aim of the present work is to develop a method which will permit the determination of the optimum vulcanization by means of the residual elongation. In the course of a study of a few types of rubber, it was observed that the residual elongation is related to the tensile strength and to the ultimate elongation.

In view of the fact that the ultimate elongation is of no particular value in characterizing a vulcanizate, the residual elongation was determined for a definite tensile strength, *viz.*, 2 kg. per sq. mm. The relation is expressed by the formula

$$\frac{\text{Residual elongation (as percentage of the original length)}}{\text{Tensile strength (in kg. per sq. mm.)}} \times 2$$

This arbitrarily chosen value corresponds to the residual elongation of rubber which has been stressed to a load of 2 kg. per sq. mm. This value is designated

hereafter as "reduced residual elongation." It is obvious that this value is wholly empirical, and there is just as much justification in choosing other values for the arbitrary load, *i.e.*, instead of 2 kg. per sq. mm., 1 kg. or 1.5 kg. per sq. mm. might have been chosen. For the sake of uniformity and ease of comparison, it is preferable to refer the results obtained to a fixed tensile strength which corresponds to the properties of most types of rubber. To this end a load of 2 kg. per sq. mm. was chosen as a standard.

To determine the optimum vulcanization, it is necessary to determine the time of heating at which the reduced residual elongation reaches its minimum value.

In the practical use of mechanical testing methods, there has for some unexplained reason been far too little attention paid to the residual elongation, and it has been utilized only for determining deformation, without any attempts to relate it to other properties, in spite of its being closely connected with the tensile strength. As a matter of fact, the residual elongation is a better criterion of the quality of a rubber sample than is the elongation at rupture.

It is possible by means of the residual elongation to determine a change in rubber resulting from deformation, for such changes are evident in a loosening of the bonds between the rubber micelles during their mutual horizontal displacement. It may be foreseen that in the case of a prolonged action, the final effect is likewise cumulative. The fact that in the new test the ultimate tensile strength may be exceeded is of no great significance, for after all an effect is involved which is also existent at lower stresses.

There is a very complicated relation between the tensile strength and the residual elongation, and within the range of ordinary vulcanization they are not directly proportional to one another. Accordingly on experimental grounds there can be no claim to great accuracy in the method of measuring the reduced residual elongation, particularly where the tensile strength is considerable below its maximum value. In such cases, the reduced value is an index of comparison only in a qualitative way, though from a practical point of view this is sufficiently precise to be satisfactory.

The reduced residual elongation is in many cases equal to zero (when the residual elongation is also zero). This condition is found only when the tensile strength is very small, *e.g.*, 0.25 kg. per sq. mm. Such values must obviously be discarded.

The results which are shown in the following section were obtained in experiments with sheets of rubber, of 2 mm. thickness, which had been vulcanized in steam under 2, 2.5, and 3 atmospheres' pressure. The residual elongations were measured after a rest of one minute, with a precision of 0.25 mm., following rupture on an Avery machine.

The residual elongations and the tensile products of all the samples of rubber were determined (see Table I and Table II).

The optimum vulcanization, calculated on the one hand from the residual elongation and on the other hand from the tensile product, frequently is not the same in the two cases, though the times are close to one another. In general the residual elongation shows the optimum time of vulcanization as a function of the tempera-

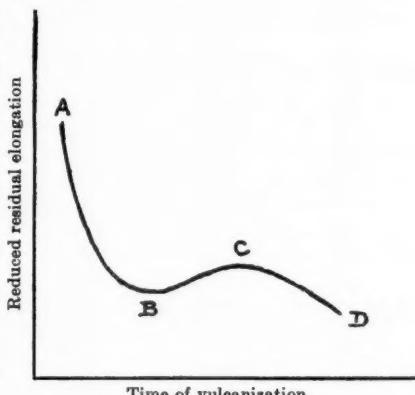


TABLE I
RESULTS OF THE MECHANICAL TESTS BEFORE AGING

Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Mm.)	Elongation at Rupture (%)	Residual Elongation	Reduced Residual Elongation	Tensile Product
Vulcanization at 2.0 Kg. per Sq. Cm. Steam Pressure					
10	0.67	740	92	275	496
15	1.00	650	21	42	644
20	1.70	655	15	18	1006
30	2.23	660	15	13	1470
60	2.37	648	19	16	1540
80	2.20	634	20.5	18	1397
100	2.19	634	20	18	1388
120	1.75	630	17	19	1100
160	1.93	590	16	17	1138
Vulcanization at 2.5 Kg. per Sq. Cm. Steam Pressure					
10	1.06	760	54	100	806
20	2.69	770	19	14	2070
40	2.37	740	20	17	1755
60	2.10	705	21	20	1480
80	2.14	688	19	18	1471
100	1.80	650	15	17	1170
120	1.81	660	12	13	1194
140	1.54	610	13	17	940
160	1.64	615	12	15	1010
180	1.41	610	9	13	860
Vulcanization at 3.0 Kg. per Sq. Cm. Steam Pressure					
10	1.07	630	20	37	674
15	2.16	670	15	14	1448
20	2.32	680	17	15	1575
30	2.42	650	21	17	1574
60	2.16	625	19	18	1350
80	2.13	630	20	19	1342
100	1.90	620	14	15	1180
120	2.14	630	17	16	1348
160	1.89	625	19	20	1313

TABLE II
RESULTS OF MECHANICAL TESTS AFTER AGING (240 HOURS AT 70° C.)

Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Mm.)	Elongation at Rupture (%)	Residual Elongation at Rupture (%)	Reduced Residual Elongation	Tensile Product
1. Vulcanization at 2.0 Kg. per Sq. Cm. Steam Pressure					
10	1.33	660	16	24	877
15	1.33	620	11	16	825
20	1.95	630	13	13	1228
30	2.21	620	18	16	1370
60	2.26	600	22	19	1356
80	2.06	530	28	28	1214
100	2.00	595	21	21	1190
120	1.62	510	24	24	826
160	1.47	510	22	22	750
2. Vulcanization at 2.5 Kg. per Sq. Cm. Steam Pressure					
10	1.29	670	17	27	864
20	2.68	650	18	13	1742
40	2.33	620	21	18	1444
60	1.86	580	20	21	1073
80	1.97	560	20	20	1102

100	1.77	550	15	17	973
120	1.53	510	14	18	780
140	1.36	495	13	19	680
160	1.33	490	12	18	651
180	1.07	455	8	15	487

3. Vulcanization at 3.0 Kg. per Sq. Cm. Steam Pressure

10	1.27	700	17	27	884
15	2.24	660	17	15	1478
20	2.32	620	21	18	1440
30	2.33	620	26	22	1445
60	1.97	580	23	23	1141
80	1.80	535	18	20	960
100	1.73	540	17	20	935
120	1.64	535	15	18	876
160	1.56	530	14	18	826

ture, in contrast to the tensile product. In this connection, it should be mentioned that the reduced residual elongation remained almost constant for widely different temperatures, and varied, as is evident in the Tables and from other experiments, between 13 and 14.

The optimum time of vulcanization, determined by the reduced residual elongation, was shorter than the optimum time determined by the tensile strength or by the tensile product, the difference in time being 10 to 15 minutes. Cases where the optimum time of vulcanization as judged by the reduced residual elongation is longer than that based on the tensile product are rarely encountered. It may be concluded therefore that the optimum time, based upon the reduced residual elongation, differs little before and after aging. On the other hand, the optimum times for a given sample of rubber, as judged by the tensile product, differ before and after aging.¹

The vulcanizates which were used in the experiments described above, and the tests of which are given in Table I, had the following composition:

Smoked sheet	48
Medium-light crepe	12
Sulfur	1.95
Mercaptobenzothiazole	0.48
Phenyl-β-naphthylamine	0.6
Stearic acid	1.5
Birch tar	0.9
Litharge	0.6
Zinc oxide	8.42
Carbon black	25.55
	100.00

The same results were obtained with other types of vulcanizates, notwithstanding the fact that the rubber content varied from 50 to 90 per cent by weight and that the other ingredients also varied.

The only fact to be noted is that the vulcanizates with a high percentage of smoked sheet showed smaller reduced residual elongations than did those with lower rubber contents. This is evident from the following results:

Vulcanizates Containing up to Per Cent	Reduced Residual Elongation
50	20-22
60	13-18
80	9.5-11.5
90	7-10

It is of course impossible to find any relation between these values, and much depends upon the other ingredients in the vulcanizates.

The residual elongation can be determined with a precision of ± 0.2 mm., and this limit of error means that the reduced residual elongation showed a variation of ± 1 , and therefore that the decimal place need not be calculated. The tensile strength and the relative elongation are also subject to errors of the same magnitude, *e. g.*, when the error in measuring the thickness amounts to ± 0.05 mm., the tensile strength is accurate only to ± 10 kg. per sq. cm. or 0.1 kg. per sq. mm. It is recognized in practical routine testing that complete agreement between two or more samples from the same vulcanizate is very improbable.

A comparison of the residual elongation and the tensile strength makes it easy to determine what mechanical tests are to be discarded. If, for example, many samples show too low tensile strengths, then the reduced residual elongation must be calculated, and if this constant for a particular sample does not vary from the normal value obtained after the same time of vulcanization, then the sample is injured, *i. e.*, it may contain creases, porosity, nicks, etc. If, on the other hand, the reduced residual elongation varies appreciably from the ordinary values, then the quality is abnormally poor for the particular type of vulcanizate.

TABLE III
OPTIMUM VULCANIZATION

Pressure of Vulcanization (in Atmospheres)	Determined by the Tensile Product		Determined by the Reduced Residual Elongation	
	Before Aging (Min.)	After Aging (Min.)	Before Aging (Min.)	After Aging (Min.)
2.0	60	30	30	20
2.5	20	20	20	20
3.0	20-30	15-20	15	15

In this way it is possible to group all samples into two classes: (1) one class comprising defective or injured samples, and (2) another class comprising samples of inherently inferior quality. Attention should be called to the well-known fact that the residual elongation varies according to whether it is measured immediately after rupture or after the lapse of a definite time. The reduced residual elongation measured after rupture varies likewise. However, this variation influences only the absolute value of this function, and does not change the relative position of the optimum. The same conclusion may likewise be drawn from the results of Kratz and Flower.²

In the course of the present investigation, it was also proved that the reduced residual elongation varies in a well-defined way with the time of vulcanization. The accompanying graph illustrates in a simple way this relation. As shown by the curve, which has an unusual character, it is obvious that the two functions are not related in a simple way. In the initial stage, the curve of the reduced residual elongation drops to a minimum (Section AB); after a slight increase (Section BC), it again falls away (Section CD). The Section CD frequently takes a zigzag course, and in many cases the reduced residual elongation reaches a still lower value, which leads to errors. The appearance of two minima is the result of over-vulcanization, and a relatively low residual elongation corresponds to the lower tensile strength. The true optimum vulcanization is established after determining the corresponding tensile strengths.³

This curve is analogous to that of Twiss⁴ for the elongation at a tensile strength of 0.5 kg. per sq. mm. This parallelism is, moreover, not a coincidence, and it may be concluded that there is some relation involved. The Section BD of the curve, which is irregular in its course, possibly may represent a disaggregation of the rubber by the heat of vulcanization, in which case this effect increases with increase in the time of vulcanization.

The work is being continued.

Acknowledgment

The author is greatly indebted to his esteemed teacher, the late Professor Buizov, for his valuable advice and his continued encouragement in the work.

References

¹ The same results were obtained with a large number of mechanical tests of about 150 different types of vulcanizates, which were carried out on the Schopper and Scott machines in the laboratory of the Scientific Research Institute of the Rubber Industry at Leningrad.

² *Ind. Eng. Chem.*, **11**, 30 (1919).

³ Eaton has also called attention to a diminution in the residual elongation with increase in the time of vulcanization (cf. Turner, *Trans. Inst. Rubber Ind.*, **2**, 6, 446 (1927)).

⁴ *J. Soc. Chem. Ind.*, **39**, 387 (1920); **40**, 242 (1921.)

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Semi-Ebonite

Part 1

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Introduction.—Hitherto two products of the reaction between sulfur and rubber have been studied and used commercially, soft rubber and ebonite. Few publications have appeared concerning the products obtained by vulcanization of proportions between 5 and 30 parts of sulfur with 100 parts of rubber.

Before the introduction of organic accelerators of vulcanization the coefficient of vulcanization was considered a satisfactory criterion of the quality of soft vulcanized rubber. Mixes of rubber and sulfur vulcanized to a coefficient of more than 3.5 to 4 were usually considered overvulcanized in that experience showed that the optimum properties as regards tensile strength and elongation at rupture occurred at this degree of vulcanization.

Semi-ebonites differ from soft rubber and ebonite in as much as they are extremely sensitive to small changes in the time of vulcanization. Their plasticity is such that the velocity of plastic flow just prior to break is relatively great, and thus they may experience a large elongation at constant load. Their plasticity decreases with further vulcanization, in fact, with advance in vulcanization they become almost rigid at room temperature. The decrease in plastic flow is accompanied by an increase in hardness and brittleness and the ultimate stage in the rubber-sulfur reaction, ebonite, is reached.

For the purpose of this investigation semi-ebonite is considered to represent a higher stage of vulcanization than overvulcanized soft rubber and is characterized by a leather-like toughness.

In the transition from overvulcanized soft rubber to semi-ebonite there appears to be an increase in internal friction which results in hysteresis during a cycle of extension and contraction with consequent sluggish recovery. The transition during vulcanization from one to another of the successive stages is not abrupt. The approximate limits of the semi-ebonite stage at normal room temperature (20° C.) are shown in Fig. 1.

The poor aging properties of overvulcanized soft rubber and its low resistance to tear render it technically unimportant. Hitherto the poor aging of overvulcanized soft rubber appears to have led to the assumption that all products intermediate between soft rubber and ebonite exhibit a like tendency to deteriorate rapidly with age. The essential differences noted between the characteristics of overvulcanized soft rubber and semi-ebonite, as defined above, suggested that there might be a corresponding difference between their behavior on aging.

The investigation outlined in the present paper was undertaken to elucidate the behavior of semi-ebonite on aging. It was later considered that the results warranted further study of the physical properties of this material, so much more readily and economically produced than the leather-like rubber products at present obtained by highly compounding rubber with fillers.

The conditions under which semi-ebonites may be obtained were first determined, and the reactions which occurred during natural and accelerated aging were in-

vestigated both as regards their chemical and their physical effects. It was also considered desirable to find whether the oxidation which occurred during aging could be retarded by incorporating small quantities of substances known to have an antioxidant effect towards the autooxidation of soft vulcanized rubber. The methods available for the mechanical testing of such tough products were reviewed and further tests improvised, which, together with an account of the volatile products of the aging of semi-ebonite will form the subject-matter for Part 2.

Preparation of Mixes.—In order to define the limits between which semi-ebonites might be obtained and to indicate the relation of these to the products of higher and lower degrees of vulcanization, a large number of mixes was prepared and cured for lengths of time ranging from 1 to 8 hours for unaccelerated mixes and 1 to $2\frac{1}{2}$ hours for accelerated mixes.

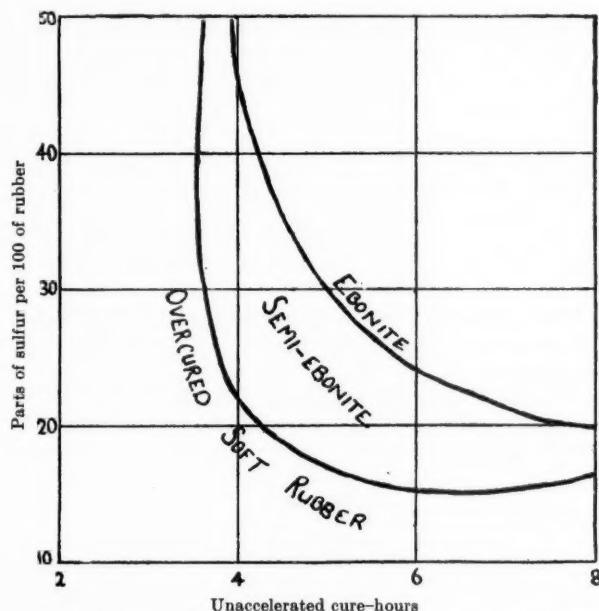


Figure 1—Approximate Limits of Semi-Ebonite Products

The procedure was the same in each case; 100 grams of pale crepe rubber were masticated for 15 minutes between rollers at about 80° C. The sulfur was introduced, a little at a time, and worked into the rubber until well dispersed in the medium. While still hot the mix was passed through the calender to give a sheet $\frac{1}{16}$ in. thick and then allowed to cool on a zinc covered bench. From the sheets rough discs were cut and trimmed to a weight of 14 grams, this amount being sufficient to fill the ring mold and yield a minimum of spew on vulcanization. The ring molds were then placed between steel sheets and vulcanized under hydraulic pressure of one ton, and at a steam pressure of 50 lb. per square inch.

Investigation of the Limiting Conditions for Producing Semi-ebonite.—Mixes were prepared containing 10 to 50 parts of sulfur per 100 parts of rubber, and these were cured for periods of 1, 2, and 3 hours.

The results are given in Table I.

TABLE I

Parts of Sulfur per 100 of Rubber	Time of Cure at Steam Pressure of 50 Lb. per Sq. In.		
	1 Hour	2 Hours	3 Hours
10-50	Grey-yellow, soft and very pliable. Tough and resistant to tearing. Higher proportions of sulfur revealed tendency to slight set. Soft Rubber	Light brown, soft but less pliable than with 1 hour cure. Firm but less resistant to tearing. Overcured Soft Rubber	Darker shades of brown. Easily torn revealing conchoidal fracture. Badly Overcured Soft Rubber

Thus a one-hour cure yielded a soft vulcanized rubber of characteristically high tensile strength and reversible extensibility with proportions of sulfur up to one-half the weight of rubber. It was observed, however, that with proportions of 25 to 50 of sulfur the product was distinctly less elastic, and after stress showed an increasingly sluggish recovery.

The two-hour cure resulted in a product of low tensile strength which, though highly resilient, broke short when stretched. This weakness became more pronounced as the proportion of sulfur was increased.

The three-hour cure produced rubbers that were obviously overcured. They tore very easily revealing a conchoidal fracture. This fracture was characteristic of all the specimens, prepared in the course of this investigation, which were found to tear easily.

It was concluded, therefore, that a longer period of vulcanization than three hours was necessary in an unaccelerated mix, for any proportions of sulfur below 50 parts per 100 of rubber.

Mixes were, therefore, prepared containing 25 to 50 parts of sulfur per 100 of rubber and these were vulcanized for periods of $3\frac{1}{2}$ to 8 hours. The results are given in Table II.

TABLE II

Parts of Sulfur per 100 of Rubber	Time of Cure at Steam Pressure of 50 Lb. per Sq. In.				$6, 7,$ and 8 Hours
	$3\frac{1}{2}$ Hours	4 Hours	5 Hours		
25	Too soft	Semi-ebonite	Semi-ebonite	Ebonite	
30	Too soft and easily torn	Trifle hard	Brittle ebonite	Ebonite	
40	Too soft and easily torn	Nearly ebonite	Brittle ebonite	Ebonite	
50	Very easily torn	Nearly ebonite	Ebonite	Ebonite	

All the samples containing more than 25 parts of sulfur per 100 parts of rubber were either too soft or too hard, though that containing 30 parts of sulfur per 100 of rubber and cured for 4 hours appeared only slightly removed in physical properties from the product required.

Of the samples containing 25 parts of sulfur per 100 of rubber those vulcanized for 4 hours and for 5 hours at steam pressure of 50 lb. per square inch proved to be good examples of the required semi-ebonite.

Examination of the samples containing 25 to 50 parts of sulfur per 100 of rubber suggested that 25 parts of sulfur was the highest that would give the desired product. Any higher proportion of sulfur tended to give an ebonite or a product approaching in physical properties those of ebonite. A shorter time of cure gave a product that was essentially an overcured soft rubber. It was considered possible that a slight

decrease in sulfur content could be compensated by an increase in the time of cure, and be advantageous in that a minimum of vulcanizing agent would diminish the possibility of dilution with free sulfur.

Further mixes were prepared containing 15 to 25 parts of sulfur per 100 parts of rubber and vulcanized for 5 hours at a steam pressure of 50 lb. per square inch, with the results given in Table III.

TABLE III

Parts of Sulfur per 100 of Rubber	Time of Vulcanization; 5 Hours at a Steam Pressure of 50 Lb. per Sq. In.
15	Black, pliable, easily torn
17.5	Black, pliable, less easily torn, little set
20	Black, pliable, fairly easily torn, more set than with 17.5 sulfur
22.5	Black, less pliable, difficult to tear, much set
25.0	Black, less pliable, very difficult to tear, much set

The specimens containing $22\frac{1}{2}$ parts and 25 parts of sulfur per 100 of rubber appeared excellent examples of the semi-ebonite product desired, the latter appearing better when warm and the former when cold.

The Effect of an Accelerator upon the Time of Cure.—As time is an important factor in industrial processes, the use of an accelerator to shorten the time of cure was an obvious economy. Vulcafor resin was selected as the accelerating agent. The results of the tests are given in Table IV.

TABLE IV

Parts per 100 of Rubber	Vulcafor Resin	Time of Cure Minutes	Observation
Sulfur			
25	2	90	Very pliable, fairly resistant to tear, some set
25	2	120	Much better product, harder, tougher, much set
20	2	120	Fairly hard, resistant to tear, considerable set
17.5	2	120	Softer, different quality. Fairly easy to tear once started. Smooth fracture
25	2	150	{ Too hard
20	2	150	

The specimen containing 25 parts of sulfur per 100 of rubber and cured for 2 hours was obviously the best of these products. It was further observed that the accelerated cure gave a series of tougher products than the unaccelerated cures.

Definition of the Product under Investigation.—The foregoing showed that a semi-ebonite was obtained when a mix containing 17.5 to 25 parts of sulfur per 100 of rubber was cured for a period from 4 to 5 hours at steam pressure of 50 lb. per square in. (148° C.). The best products were obtained when 22.5 to 25 parts of sulfur were used and the cure prolonged to 5 hours.

On using 2 parts of Vulcafor resin, semi-ebonite products were obtained with 17.5 to 25 parts of sulfur by curing for periods between $1\frac{1}{2}$ and $2\frac{1}{2}$ hours at a steam pressure of 50 lb. per sq. in. The best product of the accelerated vulcanization was obtained using 25 parts of sulfur and curing for two hours. Not only was this product visibly the best, but subsequent testing to be published in Part 2 confirmed this observation.

The accelerated cures gave better products than the unaccelerated cures. It was noted that similar proportions of sulfur with unaccelerated and accelerated mixes gave similar semi-ebonite products. This was contrasted with the soft rubbers, where considerably less sulfur was necessary with accelerated vulcanization.

The semi-ebonite products were more pliable, and more easily cut, particularly when warmed, than sole leather. In appearance they resembled ebonite, but lacked the rigidity of this material. They appeared to represent an optimum combination of the properties of flexibility and toughness.

The Effect of Natural and Artificial Aging upon the Weight of Semi-Ebonite

Preparation of Mixes.—Though 22.5 to 25 parts of sulfur per 100 of rubber yielded the best semi-ebonite products, it was decided to include mixes containing 17.5 and 20 parts of sulfur in order to cover the whole range of possible semi-ebonites. A number of experimental mixings was prepared and the mixed stocks calendered into sheets approximately $\frac{1}{10}$ inch in thickness and about 10 inches wide. These sheets were cut so that two strips slightly overlapping just filled a frame 17 inches square.

The unaccelerated mixes described in Table V were cured for 5 hours at a steam pressure of 50 lb. per sq. in. in a hydraulic press under a ram pressure of 1 ton per sq. in.

Accelerated mixes containing 2 parts of Vulcafor resin and 100 of rubber, also described in Table V, were cured for 2 hours under similar conditions. The preliminary experimental work had shown that this degree of acceleration gave products similar to those obtained with the unaccelerated mix.

The Use of an Antioxidant.—Nonox has an antioxidant effect towards the autoxidation of soft vulcanized rubber. As it has little action as an accelerator, it was decided to introduce a little of this mixture of aldol- α -naphthylamine and aldol- β -naphthylamine into one-half of each of the mixed stocks, and by companion tests estimate its influence on the aging of semi-ebonite.

Preparation of Test-Pieces.—In the first instance standard test-pieces for the Scott and Schopper machines were prepared, but this type of test was abandoned for the following reasons. Considerable difficulty was experienced in punching out ring-shaped and dumbbell-shaped test-pieces, even though hydraulic pressure was used. This involved a heavy strain on the cutters. Furthermore the tensile strength and elongation of these substances were found to be low when compared with soft vulcanized rubber, and neither the Scott nor the Schopper machines were sensitive to the slight changes in load and elongation involved when using the standard size test-piece. The character of the semi-ebonites made this type of test a far from satisfactory criterion of its value as a material for footwear.

TABLE V

Unaccelerated Mix Cured for 5 Hours at 148° C. Parts per 100 Rubber		Accelerated Mix Cured for 2 Hours at 148° C. Parts per 100 Rubber		
Sulfur	Nonox	Sulfur	Vulcafor Resin	Nonox
25	0	25	2	0
25	1	25	2	1
22.5	0	22.5	2	0
22.5	1	22.5	2	1
20	0	20	2	0
20	1	20	2	1
17.5	0	17.5	2	0
17.5	1	17.5	2	1

A flexing test is described in Part 2 of this work. It was found particularly suitable for the examination of semi-ebonites, and it was largely with this test in view that the samples were prepared in the form of sheets $\frac{1}{10}$ inch thick.

The sheets of vulcanized rubber were cut by means of a printer's guillotine into strips one inch wide and eight inches long. A small hole was pierced with a paper punch 0.4 in. from one end of each specimen. In the various aging tests the strips were suspended from glass rods pushed through these holes. This was found to be an improvement on the usual metal clip, particularly where natural aging led to the contamination of the samples with rust from the clips. The holes were designed primarily to facilitate the placing of the test-pieces in the flexing machine.

The strips were cut from the sheet in such a way that the seam was completely avoided, and each strip so numbered that similar strips from the different mixes were directly compared.

Some 30 strips were cut from each sheet.

The Effect of Overaging upon the Weight of Semi-Ebonites.—The specimens were wiped free from dust with silk and weighed very carefully. Six strips from each of the unaccelerated and accelerated mixes, 96 in all, were suspended in a Geer oven automatically maintained at 70° C. The specimens were weighed weekly and one strip from each set withdrawn for further tests.

The actual weight changes were expressed in grams per square meter of the surface of the semi-ebonite exposed and a representative series is given in Tables VI and VII, respectively, for unaccelerated and accelerated cures.

The curves representing the changes in weight are in each case similar to those in Fig. 2. It will be observed from Tables VI and VII that over a period of 7 to 9 months a definite increase in weight occurred amounting to over 10 grams per square meter of surface. Smooth curves resulted, suggesting a normal surface oxidation, with a comparatively rapid increase in weight for a short time, a marked falling off in the rate of increase as the amount of oxidizable material grew less, and an almost steady slow increase in weight for a long period.

For the purposes of easy comparison, the increase in weight per 1000 hours' aging in the oven was calculated. Table VIII gives a typical series of results summarizing 1520 determinations. These results are shown in Fig. 2.

Though the unaccelerated and accelerated cures yielded curves very similar in character, these suggest that the Vulcafor resin, used as the accelerating agent and itself a powerful antioxidant, either decreased the rate at which oxidation took place or encouraged the formation of the volatile products of the aging process in the first instance.

TABLE VI
INCREASE IN WEIGHT OF UNACCELERATED PRODUCT ON GEER OVEN AGING

Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
<i>Aging Hours</i>								
			<i>Increase in Weight in Grams per Square Meter</i>					
221	0.71	0.44	1.74	0.82	2.09	2.28	2.95	3.11
387	1.32	1.97	1.80	2.62	3.24	3.65	3.51	3.98
554	3.02	2.48	4.02	3.03	3.41	4.28	4.82	5.32
725	2.85	3.41	3.63	4.11	4.71	5.41	4.90	5.23
915	3.24	3.88	4.21	4.45	5.06	5.58	5.63	6.60
1124	3.61	4.29	4.18	5.13	4.94	6.24	6.64	7.49
2651	6.00	6.80	7.00	7.60	7.99	8.79	8.79	9.91
3058	7.02	7.06	7.62	8.16	7.83	9.01	9.68	10.78
3560	7.59	7.82	7.53	8.35	8.75	10.02	10.73	11.22
4566	7.83	8.31	8.48	9.90	9.40	10.55	11.11	11.77
5477	8.61	9.09	9.10	10.34	10.02	11.17	12.29	12.86
6173	8.97	9.42	9.61	10.92	10.42	11.78	12.40	13.25

TABLE VII
INCREASE IN WEIGHT OF ACCELERATED PRODUCT ON GEER OVEN AGING

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Aging Hours	Increase in Weight in Grams per Square Meter							
165	0.97	0.48	1.10	1.27	1.38	1.20	1.70	1.53
334	1.63	2.00	2.15	2.06	2.86	3.19	3.59	3.59
475	2.24	2.11	2.34	2.41	2.79	3.69	3.40	3.72
651	3.51	2.52	3.50	3.20	3.95	3.87	3.90	4.22
816	3.72	2.88	4.14	3.50	4.30	4.48	4.53	4.86
983	4.50	3.69	4.42	3.95	4.35	4.86	5.13	5.74
1150	4.46	4.28	4.97	4.47	5.52	5.33	5.75	6.16
1343	5.58	4.30	5.33	4.93	5.98	5.92	6.22	6.51
1505	5.81	4.79	5.59	5.01	6.17	6.01	6.49	6.77
1744	5.83	5.00	6.08	6.91	6.51	6.26	7.23	7.49
1910	6.06	5.42	6.43	6.18	7.14	6.63	7.61	8.01
2381	6.85	6.33	6.95	6.79	7.63	7.51	8.23	8.70
2715	7.75	6.41	7.78	7.62	8.26	8.44	9.07	9.55
4260	8.79	7.84	8.88	8.52	9.50	9.47	10.13	10.57
4667	8.86	8.41	9.26	8.81	9.72	9.73	10.17	10.90
5169	9.22	8.59	9.33	9.10	9.63	10.05	10.58	11.23
6175	9.71	8.82	9.96	9.65	10.59	10.62	11.08	11.92
7087	10.42	9.44	10.35	10.35	10.72	11.10	11.84	12.58
8783	10.63	9.62	10.84	10.77	11.53	11.24	11.82	12.92

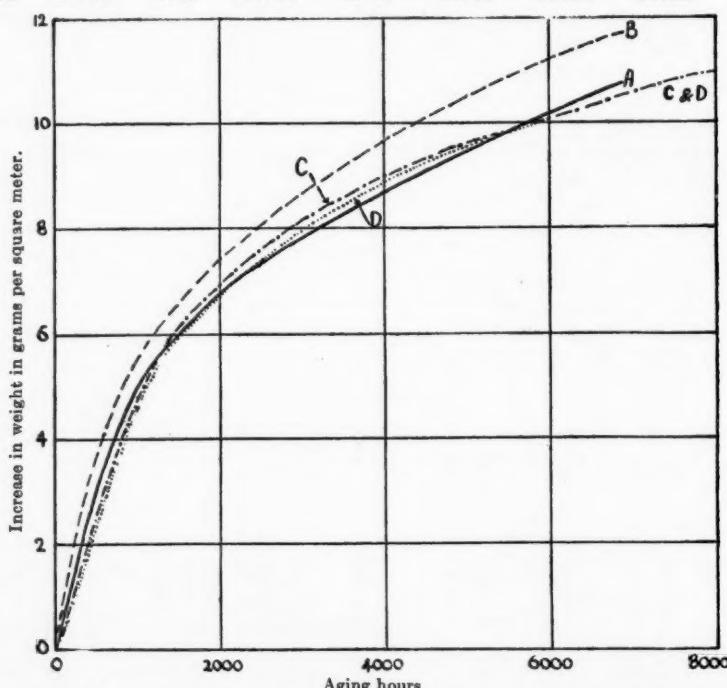


Figure 2—Increase in Weight in Grams Per Square Meter with Oven Aging at 70° C.

- A Unaccelerated product not containing Nonox.
- B Unaccelerated product containing Nonox.
- C Accelerated product not containing Nonox.
- D Accelerated product containing Nonox.

TABLE VIII

AVERAGE INCREASE IN WEIGHT IN GRAMS PER SQUARE METER
20 Parts of Sulfur per 100 of Rubber

Aging Hours	Unaccelerated Cure		Accelerated Cure	
	No Nonox	With Nonox	No Nonox	With Nonox
1000	5.00	5.52	4.72	4.58
2000	6.73	7.36	6.88	6.72
3000	7.80	8.67	8.16	8.07
4000	8.67	9.65	8.97	8.90
5000	9.43	10.52	9.60	9.52
6000	10.14	11.20	10.10	10.08
7000	10.55	10.55
8000	10.95	10.95

The lesser total increase in weight with the accelerated cure at the end of 6000 hours was attributed to a decrease in the non-volatile products of the oxidation or an increase in the elimination of volatile products.

The antioxidant, Nonox, introduced into both the unaccelerated and accelerated mixes, caused an appreciably higher increase in weight in the absence of Vulcafor resin (Fig. 2). The greater increase in weight was uniformly maintained with the unaccelerated cures, but no effect was apparent with accelerated cures.

Comparison of the curves for oven aging in Fig. 2 showed that the increase in weight for the unaccelerated cure not containing Nonox was almost the same as that for the accelerated cure with or without Nonox. Thus the presence of Vulcafor resin nullified the effect of the Nonox.

Effect of Sulfur Content on the Increase in Weight.—With unaccelerated cures, for samples with and without Nonox, the increase in weight grew less with the increase in the proportion of sulfur included. Table IX furnished clear evidence of this and attention was drawn to the percentage of free sulfur present.

TABLE IX

UNACCELERATED CURE. CHANGES IN WEIGHT IN GRAMS PER SQUARE METER AFTER 6000 HOURS' AGING

Parts of Sulfur per 100 of Rubber	Without Nonox	With Nonox	Percentage Free Sulfur on Total Weight
25	8.86	9.30	2.04
22.5	9.48	10.76	1.86
20	10.24	11.64	1.50
17.5	12.33	13.13	1.09

The presence of greater quantities of free sulfur with increase in the proportion of sulfur introduced suggested that the free sulfur was responsible for certain volatile oxidation products, leading to a lesser resultant increase in weight or a real antioxidant effect. As the curves were almost parallel after 2000' hours aging, this elimination of volatile oxidation products of sulfur probably occurred fairly early in the aging. Alternatively, the increase in the sulfur introduced rendered the product less susceptible to oxidation.

It was further observed that the effect of the antioxidant in increasing the weight became more pronounced as the proportion of sulfur was increased.

With the accelerated cures a similar but less pronounced inverse effect was readily observed (Table VII).

The Effect of Exposure to Ultra-Violet Light on the Weight of Semi-Ebonite.—The times of exposure to the rays from the mercury vapor lamp were less than those for any other aging test, and the change in weight was very small and probably within the limits of experimental error. Although the actual weight increases were

within the limits of individual experimental error, Table X is typical of a large number of determinations and may thus be accepted as indicating the effect of exposure to ultra-violet light.

TABLE X
INCREASE IN WEIGHT IN GRAMS PER SQUARE METER OF SULFUR EXPOSED TO ULTRA-VIOLET LIGHT

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Aging Hours								
					Unaccelerated Product			
5	0.361	0.273	0.343	0.388	0.370	0.423	0.361	0.361
10	0.176	0.123	0.158	0.185	0.150	0.150	0.097	0.123
15	0.194	0.167	0.238	0.238	0.220	0.282	0.158	0.167
26	0.176	0.158	0.080	0.238	0.150	0.150	0.299	0.106
					Accelerated Product			
5	0.132	0.144	0.150	0.150	0.159	0.142	0.158	0.150
10	0.185	0.176	0.194	0.114	0.160	0.097	0.123	0.132
15	0.044	-0.018	0.035	0.035	0.035	0.062	0.035	0.079

A maximum increase appeared to be reached after 5 to 10 hours' exposure, and amounted to no more than 0.2 to 0.4 grams per square meter of surface of the semi-ebonite, possibly denoting very rapid formation of a thin oxidized film on the surface of the specimen. It was noted that the surface appeared to have taken on a high polish, consistent with the formation of a very thin and hard skin. The initial small increase was followed by a slight loss in weight.

The presence of Vulcafor resin appeared to decrease the rate and extent of the increase in weight which took place. Possibly it hastened the formation of a thinner film which rapidly retarded further oxidation. Nonox had no measurable effect.

The Effect of Natural Aging upon the Weight.—Some 96 samples were suspended from glass rods attached to a framework erected upon a roof exposed to the direct action of the sun and rain. A further 96 samples were suspended below these and were protected from the direct action of the sun and rain by a wooden roof intervening.

All the samples were removed each month, lightly wiped with silk and weighed, one sample being withdrawn at each weighing.

In Tables XI and XII and Fig. 3 are recorded representative increases in weight in grams per square meter of surface which occurred during the natural aging period of 6 to 7 months.

TABLE XI
INCREASE IN WEIGHT OF UNACCELERATED PRODUCT IN GRAMS PER SQUARE METER

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Aging Hours								
					Sheltered Natural Aging			
720	1.82	1.65	1.60	2.00	1.61	2.47	1.84	2.47
1174	2.26	2.12	2.45	2.25	2.46	2.62	2.61	3.50
2736	4.07	4.07	4.25	4.89	4.56	5.15	4.81	5.98
3552	4.53	4.57	4.76	5.37	5.15	5.45	5.37	6.53
4487	5.01	4.92	5.16	6.23	5.89	6.32	6.05	7.26
Aging Hours								
					Exposed Natural Aging			
720	1.57	1.30	1.80	1.76	1.63	1.42	1.98	1.66
1174	1.20	1.09	1.46	1.09	1.09	1.08	1.22	1.88
2736	0.39	-1.20	-0.03	-0.37	-0.17	-0.40	0.74	0.98
3552	0.25	-0.83	0.88	-0.13	0.18	-0.21	0.94	1.35
4487	0.71	0.05	1.12	0.60	1.35	1.12	1.87	2.35

TABLE XII

INCREASE IN WEIGHT OF ACCELERATED PRODUCT IN GRAMS PER SQUARE METER

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Aging Hours								
Sheltered Natural Aging								
528	1.44	1.24	1.19	1.50	0.94	0.80	1.65	1.38
1153	1.26	1.28	1.29	1.46	1.46	1.73	1.79	0.92
1678	1.44	1.43	1.33	1.38	0.90	1.55	1.68	1.59
2230	2.00	1.89	1.58	1.80	1.60	2.12	2.06	2.10
2684	1.98	1.65	1.54	1.95	1.73	2.07	2.04	1.65
4246	2.09	2.61	2.65	3.02	2.71	3.15	3.02	3.34
5062	2.59	2.99	3.19	3.44	3.30	3.69	3.46	3.88
Aging Hours								
Exposed Natural Aging								
528	0.83	1.55	1.06	1.26	1.47	1.36	1.58	2.82
1153	0.55	0.34	0.66	0.40	0.55	0.21	0.77	0.13
1678	-0.69	-0.60	-1.17	-0.58	-0.99	-0.80	-1.91	-1.04
2230	-0.30	-0.05	-0.70	-0.06	-1.36	-0.95	-1.45	-0.59
2684	-0.91	-0.77	-1.72	-0.98	-2.01	-1.23	-2.12	-1.36
4246	-2.32	-0.62	-2.45	-2.45	-4.83	-3.15	-5.75	-3.78
5062	-1.67	-0.18	-2.75	-3.04	-4.48	-2.84	-4.91	-3.14

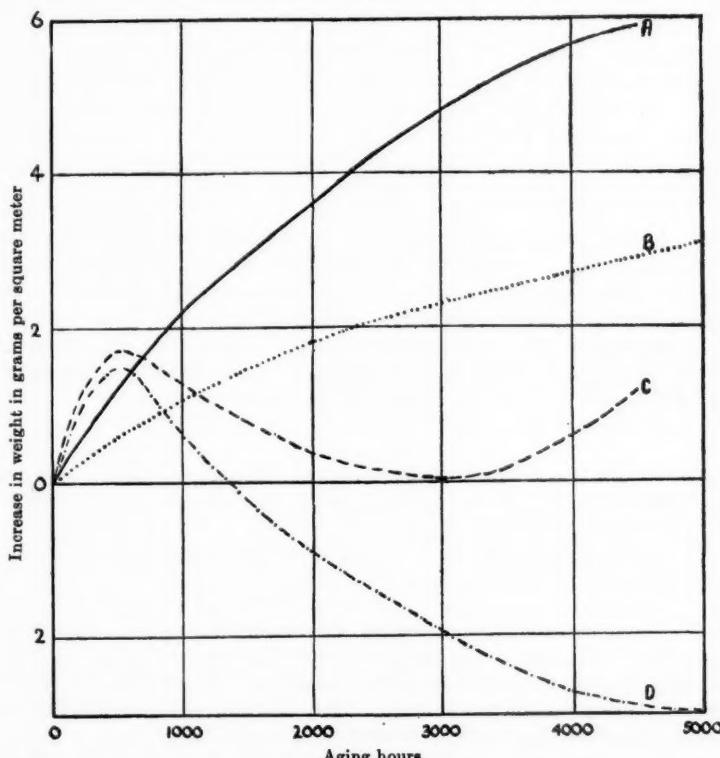


Figure 3—Increase in Weight in Grams Per Square Meter with Natural Aging

- A Unaccelerated product, sheltered aging
- B Accelerated product, sheltered aging
- C Unaccelerated product, exposed aging
- D Accelerated product, exposed aging

Marked differences were observed between the changes in weight of the specimens exposed to the action of the elements and those that were sheltered.

At the end of the aging periods the following total changes in weight in grams per square meter were obtained:

TABLE XIII

4500 Hours	Unaccelerated Cure	Accelerated Cure
Sheltered aging	5.90	2.90
Exposed aging	1.20	-2.90

Unlike those undergoing aging accelerated in the Geer oven, however, these changes were not the results of smooth increases.

For the purposes of easy comparison, Table XIV shows the increase in weight at intervals of 500 hours' natural aging and summarizes 688 determinations, of which Table XII is typical.

TABLE XIV

AVERAGE INCREASE IN WEIGHT IN GRAMS PER SQUARE METER
20 Parts of Sulfur per 100 of Rubber

Aging Hours	Sheltered Aging		Exposed Aging	
	Unaccelerated Cure	Accelerated Cure	Unaccelerated Cure	Accelerated Cure
500	1.2	0.6	1.7	1.5
1000	2.2	1.1	1.3	0.7
1500	2.9	1.5	0.8	-0.2
2000	3.6	1.8	0.4	-0.9
2500	4.3	2.1	0.2	-1.4
3000	4.8	2.3	0.0	-1.9
3500	5.3	2.5	0.2	-2.3
4000	5.7	2.7	0.6	-2.7
4500	5.9	2.9	1.2	-2.9
5000		3.1		-3.0

From Table XIV it was readily seen that the accelerating agent, Vulcafor resin, either retarded the rate at which oxidation took place by encouraging the formation of a surface protective film or it encouraged the formation of volatile products. This agreed with the result obtained with accelerated aging.

Table XV shows the effect of the Vulcafor resin on the total weight change at the end of 4500 hours' aging under different conditions, independently of the rates during particular stages (see Tables VIII and XIV).

TABLE XV

Condition of Aging	Increase of Weight in Grams per Square Meter	
	Unaccelerated Product	Accelerated Product
Hot oven at 70° C.	9.5	9.2
Sheltered natural aging	5.9	2.9
Exposed natural aging	1.2	-2.9

Thus, whatever the condition of aging, the accelerator caused a lesser net increase in weight. The increase in weight was much greater for aging in a hot oven than for natural aging. As with accelerated aging the antioxidant, Nonox, had a greater effect on the unaccelerated product than on those accelerated with Vulcafor resin, causing a noticeably greater increase in weight (Table XVI).

Effect of Sulfur Content on the Change in Weight with Natural Aging.—In Table XVI is shown the relation between the change in weight in grams per square meter after 4500 hours' aging and the amount of sulfur included in the mix (see Tables XI and XII).

TABLE XVI

Nonox Sulfur	Sheltered Aging		Accelerated Cure		Unaccelerated Cure		Exposed Aging		Accelerated Cure	
	Unaccelerated Cure	1	0	1	0	1	0	1	0	1
Increase in Grams per Square Meter										
25	5.02	4.93	2.24	2.73	0.72	0.06	-2.14	-0.50		
22.5	5.17	6.24	2.81	3.15	1.12	0.61	-2.54	-2.63		
20	5.90	6.33	2.89	3.33	1.37	1.14	-4.71	-3.06		
17.5	6.06	7.27	3.17	3.51	1.88	2.36	-5.48	-3.57		
Total	22.15	24.77	11.11	12.72	5.09	4.17	-14.87	-9.76		

Table XVI shows that the change in weight increased as the amount of sulfur present in the product decreased or as the free sulfur present decreased. The increase in weight was again observed to be greater for the unaccelerated products than for the accelerated products.

In physical properties specimens containing 25 and 22.5 parts of sulfur per 100 of rubber were very similar, and both were good examples of the semi-ebonite previously defined. Specimens containing 20 and 17.5 parts of sulfur also were similar and the latter was somewhat the poorer of the two. A corresponding similarity in the total weight changes, shown in Table XVI, was evident between these pairs of rubber-sulfur products.

It was probable that observations on the increase in weight with aging indicated some optimum mixture of rubber and sulfur yielding the best semi-ebonite products. It appears fairly certain that this optimum mixture lay between 22.5 and 25 parts of sulfur per 100 of rubber, and that any other mixture would give an increase in weight with time curve similar to but falling above or below this curve.

The Effect of Sunlight and the Humidity of the Air on the Increase in Weight.—All specimens, no matter under what conditions they were aged, showed an initial relatively rapid increase in weight. With aging in darkness and at increased temperature, the increase in weight was continued over a period of nine months. Sheltered from the direct light the general trend of the weight change with time was still an upward one. When exposed to direct sunlight the initial increase was followed by a somewhat less rapid loss in weight. This increase and subsequent loss was observed only with exposed aging (Fig. III). As this loss in weight was not observed with samples aged in complete darkness or with sheltered samples under similar conditions, the effect was assumed to be due to the effect of light, particularly sunlight.

The loss in weight could have been explained by the elimination of volatile products of oxidation, loss due to the solvent or wearing action of rain, or a fall in the humidity of the air. In view of the initial increase in weight with exposed and sheltered samples loss due to the action of rain appeared unlikely.

The Effect of Humidity upon the weight of an accelerated semi-ebonite containing 25 parts of sulfur per 100 of rubber was determined by the method, and with the apparatus, employed by Skinner and Drakeley (*Trans. Inst. Rubber Ind.*, 7, 196 (1931)).

Test-pieces 3 inches in length, but otherwise similar to those standard to this investigation, were carefully weighed under ordinary atmospheric conditions and placed in a desiccator over concentrated sulfuric acid. The apparatus was exhausted and left for four days to remove any traces of moisture at the surface of the specimens. The strips were then weighed.

The specimens were then suspended in pairs in three sealed jars over sulfuric acid of different concentrations to give humidities of 59, 83, and 100 per cent at

25° C. At the end of one week the specimens were weighed again. The results obtained are shown in Table XVII, and graphically in Fig. 4.

TABLE XVII
EFFECT OF HUMIDITY. INCREASE IN WEIGHT OF CURED SPECIMENS IN GRAMS PER SQUARE METER

25 Parts of Sulfur and 2 Parts of Vulcafor Resin per 100 of Rubber

Time, Days	0	Humidity (Per Cent)		
		59	83	100
4	-0.3			
791	1.48	2.05	

Table XVII suggested that the loss due to a fall in the humidity of the air could not exceed 0.3 gram per square meter of surface exposed. The steady increase observed with hot oven aging and the similar increase with samples exposed to dry

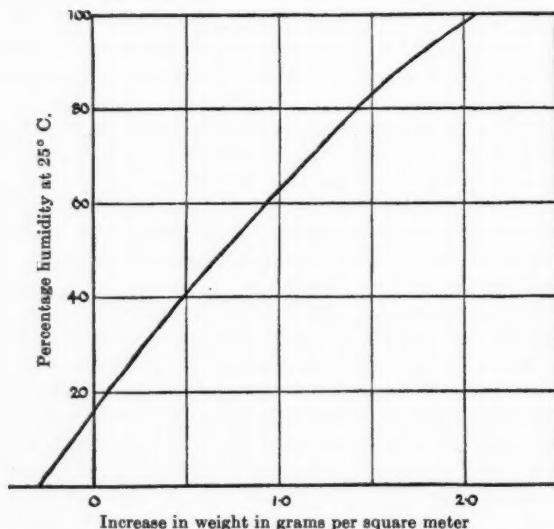


Figure 4—Increase in Weight of Semi-Ebonites Due to the Absorption of Water at Different Humidities

air at 70° C. further opposed any suggestion that changes in humidity of the air alone could account for the loss in weight with natural aging.

The increase in weight when graphed against humidity yielded almost a straight line. As 2.05 grams per square meter represented the maximum increase in weight due to the humidity of the air this cannot explain the increase in excess of this amount, the losses greater than 0.3 gram per square meter, and the difference between the increases observed with accelerated and unaccelerated cures and between sheltered and exposed aging.

It followed that sunlight assisted the loss in weight observed with exposed natural aging by encouraging the formation of volatile products of oxidation or the elimination of liquid products.

The Increase in Weight with Aging and the Formation of a Surface Oxidized Film.—

It may be reasonably supposed that the increase in weight with aging has some bearing upon the problem of the aging of rubber, and that it may throw some light upon the structure of the molecule, the stability of which must bear correlation with its susceptibility to oxidation.

As an increase in the proportion of sulfur introduced led to a lesser increase in weight with aging and a visibly better semi-ebonite product, the toughness of the latter may be associated with a lesser susceptibility to oxidation. Figures 2 and 3 suggest that the increase in weight was some indication of the amount of aging that had occurred; the action producing this change was partly or wholly responsible for the aging.

The relatively rapid increase in the first stages of the aging suggested a normal oxidation process giving rise principally to non-volatile products. The subsequent decline in the rate of increase indicated the formation of an oxidized film at the surface of the semi-ebonite which retarded further action.

Observations upon the Formation of an Oxidized Film upon the Surface of Semi-Ebonite during Aging

Considerable work has been done by various experimenters to prove and explain the existence of an oxidized film at the surface of aged rubber.

Fry and Porritt (*India-Rubber J.*, **73**, 307 (1929)) have shown that the change in color and loss in insulation properties of ebonite were due to the formation of a surface film containing acidic substances, probably sulfuric and sulfurous acids, formed by the oxidation of either free or combined sulfur. The color of the ebonite and its insulation properties were restored by surface buffing. Yamazaki (*J. Soc. Rubber Ind.*, Japan, **5**, 79 (1932); *Amer. Chem. Abs.*, **26**, 4204 (1932)); described the hardening and aging of rubber as the combined result of oxidation and polymerization, and stated that during aging some sulfur was gradually converted into sulfuric acid.

Williams (*Ind. Eng. Chem.*, **18**, 367 (1926)) and Van Rossem and Talen (*Kautschuk*, **7**, 79, 115 (1931)) noticed deep cracks when rubber was stretched and exposed to the weather. This phenomenon was ascribed to the action of ozone. Williams further discovered that light and oxygen formed an oxidized film on the surface, and that this film might protect the rubber against the action of ozone. H. A. Depew (*Ind. Eng. Chem.*, **24**, 992 (1932)) noticed that the surface of rubber exposed to the sun hardened but checked very little in six months. In time, however, the surface checked rather than cracked, this checking being a visible sign of deterioration that had occurred previously. Where the surface had been protected from the direct action of the sun little deterioration was observed. Depew attempted to measure the thickness of the surface film. He showed that deterioration continued with time of exposure but at a decreasing rate, the oxidized film exerting a protective action. This protective action was increased by the use of increased amounts of pigment.

During the aging of semi-ebonite, the following observations were made concerning the formation of a surface film.

On slight flexing, innumerable wrinkles appeared at the surface of specimens that had been aged one week in the oven at 70° C. The formation of a skin was most pronounced, as it could be made to show folds. With further aging the surface became hard and smooth. Thus, in the first week, the film was comparatively thin and wrinkled easily. With further aging the film thickened, other actions occurred and the surface cracked rather than wrinkled. The whole specimen, after one year, became rigid and brittle and snapped easily.

Naturally aged semi-ebonites showed this wrinkling effect to a lesser degree over periods of one to six months' aging. The surfaces exposed to the direct action of the sun were much sooner affected, in some cases within one month. Beyond four to six months' aging, the surface showed this wrinkling effect less and less, and beyond a natural stiffening in the cold was fairly flexible. Thus the oxidation at the surface was a slower and less complete process with natural aging, and the oxidation extended further into the rubber before the surface film seriously retarded the action. This accounted for the lesser wrinkling and continued flexibility.

In the case of the samples exposed to the direct action of the sun, the wrinkling phenomenon was followed by another peculiarity. The specimens were distinguished one from another by symbols inked on the surface. The symbols were usually bleached by the sun or worn away almost completely during a month's exposure. This necessitated further inking. It was observed that the fresh ink was absorbed by the surface and was inclined to spread as on blotting paper. This suggested that the surface film suffered disintegration and allowed further oxidation to take place more readily. This may explain the loss in the second stage of the weight change with time curves for exposed natural aging, for neither the bleaching nor the absorption was noticed to any marked extent with the sheltered specimens, and suggests that sunlight encouraged disintegration at the surface.

The short periods of exposure to ultra-violet light gave rise to a smooth polished surface on the specimens of semi-ebonite. Here, too, the surface wrinkled on flexing although it was such as to suggest the rapid formation of a very thin and relatively hard film.

It was decided to prove conclusively whether the surface film had retarded the oxidation of the semi-ebonite.

Several samples that had been aged for 12 months in the Geer oven were cut transversely into two parts. One portion of each was suspended in the oven to age as before. The remaining portion of each was cut into 9 strips to provide a freshly exposed surface, enclosed in a wide glass tube open at both ends and placed in the oven with the first set of samples. After 20 days all the samples were removed from the oven and weighed again.

In Table XVIII, the increase in weight has been calculated in grams per square meter of surface of the semi-ebonite and compared with the increase shown in the 425 hours of aging immediately prior to the cutting (from Table VII).

TABLE XVIII
THE INCREASE IN OXIDATION WITH EXPOSURE OF FRESH SURFACE OF ACCELERATED PRODUCT

Sulfur Nonox	25	25	22.5	22.5	20	20	17.5	17.5
Aging	Increase in Weight in Grams per Square Meter							
425 hours prior to cutting	0.05	0.05	0.17	0.10	0.20	0.04	0.00	0.09
480 hours after cutting	3.50	2.68	4.18	2.97	3.47	3.33	2.67	2.01

Thus, while the uncut portions showed practically no change in weight, the freshly exposed portions showed a substantial increase. This proved that the oxidized film at the surface of the rubber almost entirely prevented the oxidation of the interior. As a fresh surface was exposed the oxidation was renewed, presumably leading to the formation of a further oxidized film.

In Table XIX the increase in weight with fresh exposure is compared with the initial increase in weight (from Table VII).

TABLE XIX

INITIAL INCREASE IN WEIGHT WITH ACCELERATED AGING AND THE INCREASE IN WEIGHT OF THE SAME SAMPLES WITH A SURFACE FRESHLY EXPOSED ONE YEAR LATER

Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
Aging								
	Increase in Weight in Grams per Square Meter							
Initial 475 hours	2.24	2.11	2.34	2.41	2.79	3.69	3.40	3.72
480 hours one year later	3.50	2.68	4.18	2.97	3.47	3.33	2.67	2.01

Table XIX shows that the exposure of a fresh surface one year later led to a further increase in weight of the same order as the initial increase in weight. This indicates the effectiveness with which the film had prevented further oxidation of the interior, and suggests that oxidation under the given conditions was almost exhausted after one year's aging.

The Effect of Different Aging Conditions upon the Formation of the Surface Film.—The initial relatively rapid increase in weight suggested a possible measure of the effect of different aging conditions in promoting the formation of the surface oxidized film.

For each aging test, the average initial rate of increase in weight in grams per square meter per 100 hours' aging was read from Figs. 2 and 3 and the results entered in Table XX.

TABLE XX

THE INITIAL INCREASE IN WEIGHT PER 100 HOURS, UNDER DIFFERENT CONDITIONS OF AGING, CALCULATED IN GRAMS PER SQUARE METER

Cure	Hot Oven	Sunlight	Shade
Unaccelerated	0.46	0.34	0.24
Accelerated	0.45	0.30	0.12

These results suggest that heat promoted the formation of the oxidized film at the surface of the semi-ebonite more effectively than sunlight, and that oxidation proceeded less rapidly when the specimens were protected from direct sunlight. The accelerator appeared to retard slightly the formation of the surface film.

Yamazaki (*loc. cit.*) showed that the acetone extracts of products not very different from those employed in this investigation were high in summer and winter sunlight at 60° C. and low for either season at 20° C. The extract reached a maximum with the greatest light intensity and with the highest temperature. A decrease in the extract occurred with prolonged exposure and was attributed to further oxidation and polymerization to substances insoluble in acetone.

Thus, whether the oxidation at the surface be measured by the increase in acetone extract or by the increase in weight with aging similar conclusions regarding the effect of heat and light in promoting this oxidation may be drawn.

Increase in the Ratio of Combined Sulfur to Free Sulfur with Decrease in the Sulfur Introduced into the Mix.—The percentage of free sulfur present in the different samples of semi-ebonite immediately after vulcanization was determined by extracting shredded portions of the specimens with hot acetone. The combined sulfur was calculated as the difference between the sulfur introduced into the unvulcanized mix and the free sulfur present in the vulcanized product, the small losses during press vulcanization being ignored.

The ratio between the combined sulfur and free sulfur present with curing under similar conditions was calculated, and is shown in Table XXI.

Parts of Sulfur per 100 of Rubber	Parts per 100 of Vulcanized Products			Ratio Combined Sulfur Free Sulfur
	Total Sulfur	Combined Sulfur	Free Sulfur	
25	20	17.66	2.34	7.5
22.5	18.37	16.51	1.86	8.9
20	16.67	15.17	1.50	10.1
17.5	14.89	13.80	1.09	12.7

Table XXI shows that the proportion of total sulfur which combined with the rubber diminished as the actual amount of total sulfur introduced into the mix increased. This may have indicated the gradual approach to the stable intermediate saturation product of rubber, semi-ebonite, or merely to the limit of solubility of sulfur in the hot rubber. In either case the increased toughness may be associated with the increased proportion of uncombined sulfur. This may explain the obviously greater toughness of the accelerated cures, as the introduction of Vulcafor resin led to similar vulcanization products containing less combined sulfur.

Semi-Ebonite and the Sulfides of Rubber

The bulk of the evidence available favors the theory that a progressive combination between sulfur and rubber occurs during vulcanization. The rate at which this reaction proceeds may be increased by an increase in the amount of sulfur introduced into the mix. Table XXI shows that the proportion of total sulfur which combined with the rubber diminished as the actual amount of sulfur introduced into the mix decreased, suggesting that the rubber grew less susceptible to sulfuration as vulcanization proceeded.

The evidence obtained regarding the change in weight of semi-ebonite with aging showed that the increase in weight diminished with the amount of combined sulfur present. The product therefore grew less susceptible to oxidation as vulcanization proceeded.

The better semi-ebonites, obtained with 22.5 to 25 parts of sulfur per 100 of rubber, were, therefore, those stable vulcanized products intermediate between overvulcanized soft rubber and ebonite, which were least susceptible to oxidation and sulfuration.

Ebonite contains 32 per cent sulfur and has an empirical formula $(C_{10}H_{16})S_2$. If the best semi-ebonite be represented by the formula $(C_{10}H_{16})S_n$ and the proportion of combined sulfur taken to be 17-18 per cent (see Table XXI), then n is almost equal to unity. Thus the empirical formula for semi-ebonite is $(C_{10}H_{16})S$.

Assuming that the simplest sulfide, soft vulcanized rubber, involves the saturation of the double bonds at the ends of the rubber molecule, the empirical formulas for semi-ebonite and ebonite, respectively, suggest that the double bonds in the molecule may be saturated in two stages.

It is suggested, therefore, that between the two stable sulfides, soft vulcanized rubber and ebonite, there is an intermediate reasonably stable sulfide described in this investigation as semi-ebonite.

Part 2 of the paper will be submitted for publication shortly.

Acknowledgment

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Fatty Acid Softeners in Rubber Compounding

C. M. Blow and T. L. Garner

Literature has been published dealing with the properties and characteristics of the fillers, accelerators, and antioxidants used in rubber compounding, but the field of the so-called softeners and dispersing agents has been very largely neglected. In fact it is scarcely possible to find evidence of any systematic work (see Appendix 2) on this class of compounds, which are likely to be of increasing importance in rubber compounding. In addition, as far as could be ascertained, no established technic for their investigation exists. In this paper, therefore, an attempt is made in the first place to describe in outline a method for the study of softeners in general, and secondly to discuss in particular the behavior of a series of fatty acids and their salts.

In rubber compounding, softeners are added for three main purposes: to reduce the mastication time and assist processing; to aid the dispersion of pigments, particularly carbon black, and to activate accelerators. From the point of view of a tire tread stock, the property of the softener to produce a very high degree of dispersion of the carbon black in the rubber may be its most important function, the suggestion being that the higher the degree of dispersion the more resistant to abrasion and flexing the stock becomes. At the same time a certain degree of softness and tackiness is required for processing, and the mix will probably contain an accelerator that needs activating. The ideal softener would be one performing all three tasks.

In this paper it is not proposed to deal at any length with the activation of accelerators, and therefore the problem divides itself into two parts. In the first place the softening action of any suggested softener is required to be measured, quantitatively, if possible. A plasticity test will be described shortly that appears to achieve something in this direction for a given set of conditions. In the second place the dispersion of carbon black produced by the softener has to be studied, and parallel with this, correlating measurements of abrasion resistance and flexing resistance have to be made. A microscopic method was adopted for the actual study of dispersion, and will be described and illustrated.

Mixing and Curing Procedure.—The composition of the mix was as follows: smoked sheet rubber, 100 parts; carbon black, 40; zinc oxide, 5; sulfur, 3; accelerator (mercaptobenzothiazole, $\frac{5}{8}$ or diphenylguanidine, $1\frac{1}{4}$) and softener, 3 parts.

To eliminate as many errors as possible, master batches were first mixed from a blend of raw rubber. Roughly equal portions from each of four cases of smoked sheet (from different estates) were batched in four approximately 100 pound batches. In this way, there was available between 400 and 500 pounds of blended rubber.

Two black master batches (*A*) of the composition: rubber 103 and carbon black 48, were then mixed; a master batch (*B*) containing zinc oxide, and sulfur of the composition, rubber, 50; sulfur, $18\frac{3}{4}$; zinc oxide, $31\frac{1}{4}$; and a master batch (*C*) containing the accelerator, and having the composition either 80 parts of rubber with 20 of diphenylguanidine or 90 parts of rubber with 10 parts of mercaptobenzothiazole.

Quantities of the master batches were taken as follows: *A*, 1465 g.; *B*, 185 g.; *C*, 72.5 g., and blended on a 12 in. diameter roll laboratory mill with the incorporation of the softener under investigation; 35 g. corresponding to 3 per cent on the rubber content of the mix. Master batch *A* was warmed for 10 to 12 minutes; a small portion (*a*) was removed for plasticity and dispersion tests; then the softener was added, the time taken for this being as a rule 5 minutes. A small sample (*b*) was removed for plasticity and dispersion tests, and the master batches *B* and *C* were then blended for 4 minutes. The mix was sheeted out for curing tensile test-pieces, and abrasion and flexing pieces.

The mixed rubber was allowed to stand for a period of at least 24 hours before curing. All curing was carried out at 280° F. in a double daylight hand screw press. Cured samples were tested within a period of from 36 to 96 hours after curing.

Softening Action

Plasticity measurements were considered to be the most satisfactory, being comparatively easily made, and as reliable as other procedures employed in this investigation.

The test consisted of measuring the time taken to compress a pellet (1 sq. cm. in cross-section, and 1 cm. long), between platens of 1 sq. cm. cross-section, from a thickness of 7.5 to a thickness of 5 mm. under a load of 1000 grams at 100° C. The pellets were preheated 15 minutes.

This test was carried out in duplicate on the samples "*a*" and "*b*" (referred to above) from each mix. In addition, measurements were made of the variation of plasticity with the time of milling of the black master. On the resulting curve (Fig. 1) the calculation of the quantity "softening action" is based.

The plasticity figures for "*a*" and "*b*," which give the softness of the black master just before and immediately after addition of softener, respectively, can be expressed (by means of the curve) as representing so many minutes' mastication of the black master. Then the difference between these quantities, less the time taken to add softener, is a measure of the "softening action" of the substance.

This can be illustrated by taking an example to be considered in conjunction with Fig. 1. Suppose "*a*" to have plasticity of 29 sec., and "*b*," 8.5 sec., and the time taken to add the softener, 5 minutes. These figures for plasticity correspond, respectively, to 11 and 26 minutes' mastication of the black master (*A*). The softening action is therefore (26 - 11 - 5) or 10. This figure is necessarily not absolute, but its method of calculation appears to give at least a quantitative comparison between softeners, providing the conditions on the mills are maintained constant, and one black batch is used throughout. Furthermore, the softening action is measured in terms of the very property concerned, that is, the reduction of mastication time.

It should be added here that several curves were obtained for the black master, but these only differed in respect to their positions, and they could be brought together by moving horizontally only. This difference is of course due to slight variations in treatment during the initial stages of warming.

It is necessary, however, to consider what factors are likely to influence the figure obtained for any particular softener. They are, assuming the percentage of softener constant and a uniform rubber, treatment on the mill, time of addition of the softener, and time of milling before addition of softener.

It was, however, found possible by careful control of the milling technic to obtain reasonably constant results. Further, the time of addition of the softener appeared to be without effect, providing the actual time of addition was used in arriving at the softening figure. Table I gives data to substantiate this conclusion.

TABLE I
Softner: 3% Stearic Acid

Time of addition of softener, min.	3	5	8
Softening action	12.5	12.0	11.5

The time of milling before addition of the softener also had little effect within the narrow range of 10 to 12 minutes' premilling in the experiments. Outside these limits there was some variation, as shown in Table II. Where necessary, correction was made to a standard of 11 minutes' premilling. (It is to be noted that the time of milling was arrived at from the plasticity of sample *a*.)

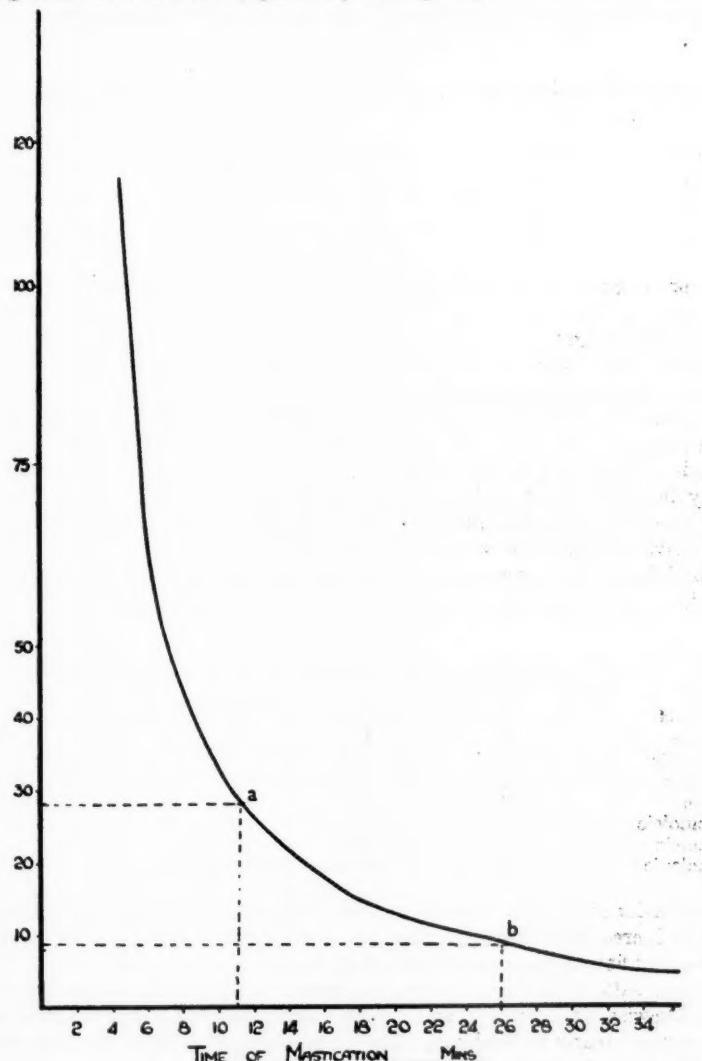


Figure 1—Effect of Time of Mastication on the Plasticity

TABLE II

Softner: 3% Stearic Acid Added in 5 Min.

Time of milling before addition, min.	7	11	12	13	13½	16
Softening action	16½	12	12	11½	11	8½

Figures were also obtained for the softening action of increasing percentages of a softener. Table III gives data for 1, 2, 3, and 4 per cent of stearic acid, zinc laurate, zinc stearate, and pine tar oil, and reveals that the relation is not strictly linear. Further work is undoubtedly required, but it appeared that, first, in some cases a certain percentage was necessary to be effective and, secondly, above a certain percentage it was uneconomical to add more of that particular softener.

TABLE III

SOFTENING ACTION OF SOFTENERS ADDED IN 5 MIN. AFTER 11 MIN. PREMILLING

Per Cent	Softening Action			
	Stearic Acid	Zinc Stearate	Zinc Laurate	Pine Tar Oil
1	3½	0		7
2	7½	1	11½	9½
3	12½	3½	14	13
4	12½	4	22½	16½

It is proposed to describe the effect of increasing unsaturation in fatty acids, and their salts, on their properties in rubber compounding. The series chosen consisted of the straight chain fatty acids, containing 18 carbon atoms: stearic, fully saturated; oleic, with one double bond; linoleic, with two double bonds; and linolenic with three double bonds.

To extend the scope, lauric, palmitic, and ricinoleic acids were also studied.

In addition to the acids, the zinc, magnesium, and barium salts, and the triglyceride of each acid were investigated. The mixing and testing procedure was as already described; 3 per cent of softener on the rubber being employed throughout. In the case of the salts an additional percentage was however added, so that chemically equivalent quantities were always present.

Table IV gives the corrected figures for the softening action of all the compounds studied.

TABLE IV
SOFTENING ACTION OF FATTY ACIDS AND SALTS

3% of	Acid	Zinc Salt	Magnesium Salt	Barium Salt	Glyceride
Lauric	5	14	10½	4½	13
Palmitic	8½	4½	1½	...	
Stearic	10½	3½	3	0	11½
Oleic	8	18½	11½	2½	10
Ricinoleic	9	11½	3½	1½	6
Linoleic	13	10½	10½	0	
Linolenic	12	10½	8½	...	13½

The conclusions to be drawn are that of the acids, the series lauric, palmitic, stearic, shows an increasing softening action, also oleic, linoleic, and linolenic; but stearic acid does not fit into the series stearic, oleic, linoleic, and linolenic.

The zinc salts of lauric, palmitic, and stearic acids show a decreasing softening action, likewise oleic, linoleic, and linolenic acids, but again zinc stearate does not fit the series, stearic to linolenic. The magnesium salts follow the zinc salts, but with a diminished softening action.

The barium salts, on the average, have very little softening action.

The glycerides show no great regularity, but appear to have a marked softening action in many cases.

The effect of a hydroxy group (ricinoleic) is to give a fairly uniform reduction, except in the case of the acid itself.

To supply standards for comparison, Table V gives data obtained on several common softeners.

TABLE V
SOFTENING ACTION OF OTHER SOFTENERS (3%)

Pine tar oil	13	Mineral rubber	$4\frac{3}{4}$
Cottonseed oil	10	Paraffin wax	$8\frac{3}{4}$
Mineral oil	$7\frac{1}{2}$	Higher aliphatic alcohol	$16\frac{1}{4}$

Purity of Substances.—Wherever a technical or commercial product was readily and cheaply available this was employed. Other products were prepared as detailed below. No great purity was aimed at, but recrystallization of salts was carried out wherever this was possible. The salts were prepared from the acids by the reaction of the acetate of the metal with the potassium salt of the fatty acid. By careful control of alkali concentration it was possible to obtain products free from metallic oxide, though a check of the ash was carried out as a rule to ensure that this was so. In the case of the linoleic and linolenic acids, it was not possible to purify the salts on account of their resin-like character.

Lauric acid and zinc laurate were commercial products. The magnesium and barium salts were prepared from the acid, and hardened cocoanut oil was used as containing a high percentage of trilaurin.

Technical palmitic acid was purchased and used for the preparation of the zinc and magnesium salts.

Stearic acid and zinc stearate were commercial products, from which the magnesium and barium salts were prepared. The tristearin was a technical product.

Oleic acid, zinc and barium oleate were all technical products. The magnesium salt was prepared from the acid, and the glyceride by heating the acid with glycerine and purifying with alcohol.

Ricinoleic acid and salts were prepared from commercial castor oil, which was taken as the glyceride. The barium salt was used to purify the crude acid obtained by saponification.

Linoleic acid was purchased and the salts prepared from it. Linolenic acid consisted of the unpurified acids obtained by saponification of linseed oil, which was used as the glyceride. The salts were prepared from this acid.

In Table VI are given the melting points (or softening points, in the case of certain of the resinous products) of the substances, for which the softening action has been determined.

TABLE VI
MELTING POINTS OF SOFTENERS (° C.)

	Acids	Zinc Salts	Magnesium Salts	Barium Salts	Glycerides
Lauric	24°	110°	98°	Indefinite	30°
Palmitic	56°	107°	160°
Stearic	60°	116°	107°	Indefinite	53°
Oleic	Liquid	102°	Semi-liquid	Decomposes	Viscous liquid
Ricinoleic	Liquid	65°	95°	103°	Liquid
Linoleic	Liquid	78°	Gum	Indefinite	...
Linolenic	Liquid	76°	71°	...	Liquid

It will be seen that no relation exists between the melting point and the softening, except that the barium salts all have high melting points and little softening action.

With regard to the ease with which the various substances milled into the rubber, it may be stated that all were easily handled except barium oleate, which could not be made to disperse sufficiently to enable non-porous cured samples to be prepared; and castor oil, which could only be mixed with difficulty.

Dispersing Action

The second part of the investigation described in this paper concerns the effect of these softeners on abrasion and flexing resistance, and as dispersing agents for carbon black, with an attempted correlation of the two properties.

Choice of Mix.—For the softening action measurements, the only substances concerned were the black master batch (*A*) and the softener under investigation. In the subsequent part of the work, however, a mix containing zinc oxide, sulfur, and accelerator was essential, and details of the mixes (*B*) and (*C*) have already been given.

It was originally intended to use for this investigation a mix accelerated by mercaptobenzothiazole on account of the known excellence of this accelerator for high abrasion resistance, but the problem arose of trying to cure a mix of this type in the absence of stearic acid or some other fatty acid.

A few experiments were carried out with stearic, lauric, and ricinoleic acids, their zinc and barium salts and glycerides. With the exception of stearic and lauric acids, and their zinc salts, very low tensile and poor abrasion figures were obtained, and it was impossible to be sure that these were not due to incomplete vulcanization.

The only alternative seemed to be to use diphenylguanidine, which will cure without the presence of the substances required by mercaptobenzothiazole. To bring the rate of cure within reasonable limits it was found necessary to employ $1\frac{1}{4}$ per cent of diphenylguanidine, compared with $\frac{5}{8}$ per cent of mercaptobenzothiazole.

Tensile Measurements.—It was thought necessary to carry out routine measurements of tensile strength on all the experimental mixes in order to obtain an approximate figure for optimum cure, and to ensure that no great change was produced in this property.

It is not proposed to give any definite data, but Table VII is a summary of the results obtained with the same series of compounds, as used for the experiments on softening action. The accelerator for the mixes was diphenylguanidine, and the amount of softener was 3 per cent.

TABLE VII
EFFECT OF SOFTENER IN TENSILE STRENGTH AND TIME OF VULCANIZATION

No Softener:	Tensile Strength at Break 280 Kg. per Sq. Cm.	Time of Optimum Cure at 280° F. (Min.)	
		60	
Acids	Reduced by 12-16%	Retarded by 20-30	
Zinc salts	Reduced by 10% of linoleic and linolenic acids by 16%	Ditto	
Magnesium salts	Ditto	Retarded by 10-15	
Barium salts	Small effect only	Accelerated by 5-10	
Glycerides	Reduced by 14% (Except Triolein: Reduced by 7%)	Slightly retarded	

Abrasion-Resistance Measurements.—In the measurement of abrasion resistance the machine, as standardized by the Research Association, was used with no altera-

tion in technic. As a general rule, abrasion tests were carried out for 3 or 4 cures, and the best figure taken. The cure giving the optimum figure corresponded in most cases very closely to the optimum cure obtained from tensile strength measurements.

Table VIII gives the abrasion figures obtained on a series of fatty acids and their salts. The figure is the loss per cent by weight of the specimen per 1000 revolutions of the abrasive wheel. In all cases diphenylguanidine was the accelerator.

TABLE VIII
FIGURES FOR ABRASION LOSS FOR MIXES CONTAINING 3% OF FATTY ACID OR SALT

	Acid	Zinc Salt	Magnesium Salt	Barium Salt	Glyceride
Lauric	1.09	1.12	1.38	1.31	1.38
Palmitic	1.18	1.13	1.24
Stearic	1.16	1.17	1.28	1.29	1.38
Oleic	1.29	1.21	1.44	..	1.33
Ricinoleic	1.44	1.37	1.56	1.46	1.37
Linoleic	1.34	1.54	1.53	1.70	..
Linolenic	1.45	1.55	1.69	..	1.43

Containing no softener 1.40

The main conclusions are that with the acids there was a decrease in the abrasion resistance with unsaturation from stearic to linolenic. The effect of the hydroxy group is to decrease abrasion resistance. A similar behavior is observed with the zinc salts, the rise of abrasion loss with unsaturation being steeper; linoleic and linolenic gave figures above those for the blank. The magnesium salts were similar in action to the zinc salts, but gave poorer figures. The barium salts, in several instances, produced lower resistances to abrasion than the blank mix containing no softener. The glycerides gave figures in the neighborhood of the blank mix.

Effect of Temperature on Abrasion Loss.—As tire treads in practice run at temperatures considerably above that of the surrounding air, it seemed desirable to obtain abrasion data at temperatures above the normal. To this object the abrasion machine was enclosed in an asbestos box fitted with a 600-watt electric heating element, by which means the sample and abrasive wheel could be maintained at any temperature up to 120° C. (See Fig. 2).

Altogether six different mixes were studied, and in five cases the results showed a diminution of abrasion loss, that is, improved resistance to abrasion with rise of temperature. In Table IX, the results are given.

A possible explanation of the figures was that the result was a characteristic of the machine and not the rubber. (See Appendix 1.) Therefore, a further experiment was carried out using an actual cycle tire mounted on a wheel running at a

TABLE IX
ABRASION LOSSES AT VARIOUS TEMPERATURES

Temperature, ° C.	Abrasion Loss, %	Temperature, ° C.	Abrasion Loss, %
<i>Motor tire tread (black) stocks:</i>			
22	0.895	20	1.08
45	0.843	50	0.94
55	0.715	75	0.82
85	0.53	105	0.68
108	0.454
<i>Cycle tire tread (black) stocks:</i>			
20	1.94	20	1.46
60	1.25	60	0.935
95	0.673	95	0.545
<i>White tire stocks:</i>			
<i>Hard (80 Shore)</i>		<i>Soft (46 Shore)</i>	
20	2.34	20	2.90
90	3.35	100	1.47

slight angle on the surface of a large wheel covered with abrasive, the whole being enclosed.

The temperature inside the box was raised to 55-60° C., and duplicate tests were run at this temperature and at room temperature. Good agreement was obtained, and the results are given in Table X.

TABLE X
FIGURES FOR ABRASION LOSS ON CYCLE TIRE

Tire pressure 30-35 lb. per sq. in. Load, 100 lb. Angle, 10°. Abrasive, Oakey's Emery No. 1 (blue back). Run for 30 min. at 18 m.p.h.

Temperature °C.	Loss, G.	
Room temperature	93	93
55-60	55	58

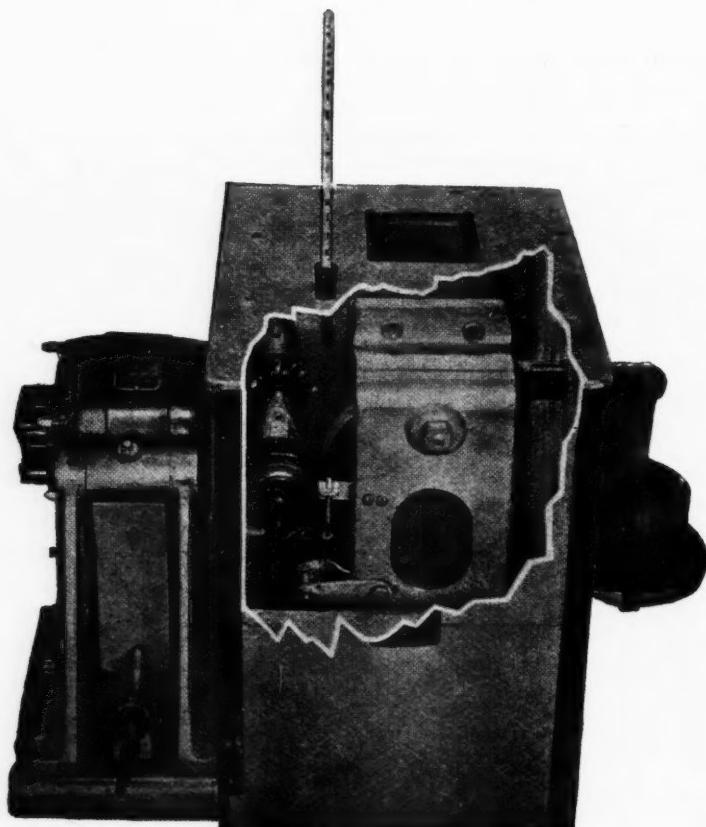


Figure 2

One further observation is worth recording. The sample from the abrasion machine showed, on the abraded surface, an even and definite grain, rather like a

fingerprint, in appearance, which was the same for the same mix under the same conditions. It was observed that with a rise in the temperature of abrasion the grain became finer. Figure 3 illustrates this in the case of one of the mixings. A finer grain indicated that smaller particles were removed. Now it might be considered that abrasion and the detachment of particles are due to innumerable cuts, and further that at high temperatures the rubber is tackier, with the result that cuts tend to be sealed up more readily. The result of this resealing tendency is to render the cuts less deep, and the detached particles smaller.

The results on abrasion at high temperatures and the above explanations are put forward with some hesitation, and only to suggest that further work in this direction

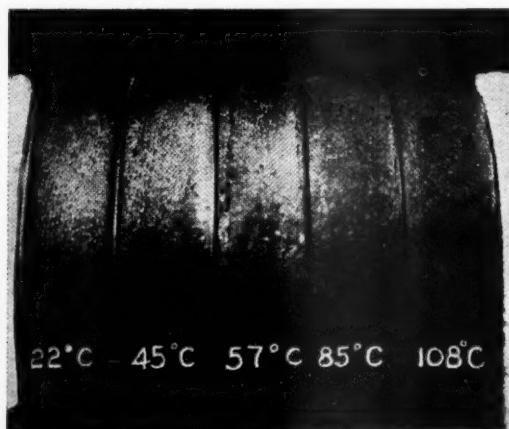


Figure 3

is desirable. One point is obvious, and that is that any laboratory experiments on abrasion must take temperature into account. This has been the case in the results recorded above.

Flexing Tests.—For flexing tests, test-pieces of the shapes shown were cured on to a canvas backing, and fastened to a standard length belt, which ran on a three-pulley system illustrated in Fig. 4.

All the test-pieces on any one belt were cured in the same mold cavity; each belt carried eight pieces, and a system was worked out whereby each mix at its required cure, or cures, was vulcanized in different cavities, and tested on at least three belts. The belts were run regularly for 30-minute periods with 10-minute intervals, to allow for cooling of samples, which tended to heat on flexing. At intervals the test-pieces were inspected. The order taken was that in which the cracks develop on the test-pieces, rather than the order in which the pieces became cut through. Data were obtained on the flex-cracking of the series of mixes on which the abrasion tests (Table VIII) were carried out. A flexing index is used to represent the resistance to flex-cracking. A high figure indicates poor resistance, and a low figure good resistance. The data on this basis is given in Table XI. But it should be noted that the change in flexing-resistance from an index of 5 to one of 8 represents a greater difference than that between indices 1 and 4.

TABLE XI
FLEXING INDICES FOR MIXES CONTAINING 3% OF FATTY ACID OR SALT

	Acid	Zinc Salt	Magnesium Salt	Barium Salt	Glyceride
Lauric	4	2	6	7	3
Palmitic	4	3	7
Stearic	3	1	6	8	4
Oleic	5	3	5	8	4
Ricinoleic	5	8	7	7	7
Linoleic	6	6	8	8	..
Linolenic	7	7	6	8	5
			(Soft)		(Soft)

Blank. No softener 8

The factors affecting flexing properties appear to be as follows.

Surface Condition of Rubber before Curing.—In all the experiments reported here, the rubber was freshly cut, and was molded without lubricant or chalk. It was found that a chalked surface might produce a test-piece with a life as low as one-half that of a clean molded piece.

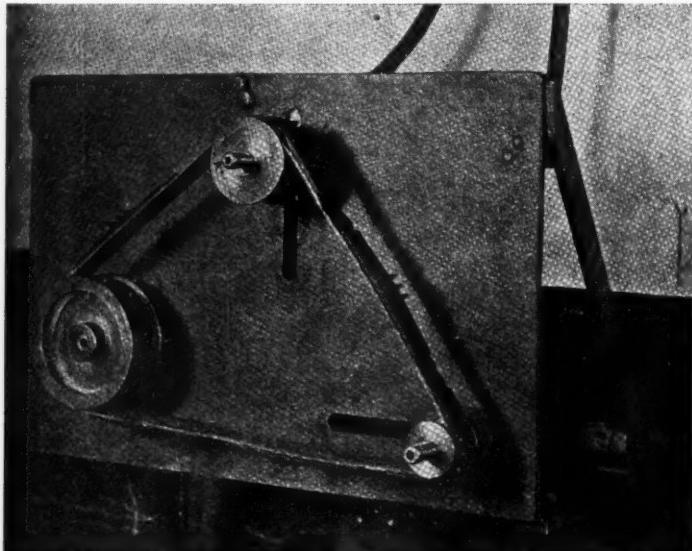


Figure 4—Flexing Machine

Pulley diameters $3\frac{3}{4}$ in. (1350 r.p.m.); $2\frac{1}{4}$ in.; $1\frac{1}{4}$ in.
Length of belt (8 pieces), 38 in. Hence each test piece has 1275 flexings per minute or 425 at each pulley.

Hardness.—The pulleys of the flexing machine being fixed, are set in a position so that the belt is taut. This diminished considerably the tendency for the softer (more pliable) pieces to follow the shape of the pulley more closely than the harder ones, and so to be subjected to more flexing action. Undoubtedly, the more flexible the test-pieces the more flexing they received, but this was reduced to a minimum by having a taut belt on fixed-position pulleys. Certain of the substances investigated as softeners produced a definite softening of the cured stock. This

softening might account for improved flexing resistance, but a hard mix might also give an erroneously good flex resistance due to the operation of the factor mentioned.

State of Cure.—This factor is connected with hardness in that an undercure yields a softer mix, and one on which less work is done, than with an overcure. Generally speaking, resistance to flex-cracking decreased with increase of cure, but this variation itself varied from mix to mix.

The data recorded above refers to the flex-cracking at the cure giving optimum abrasion resistance, and tensile properties. In some cases, however, where the decrease of flexing resistance with cure was very marked, the index was depressed a point. This appeared justifiable on account of its importance from the practical point of view.

Experiments on Flexing at High Temperatures.—Flexing tests run at room temperature, 65° C. and 100° C., did not yield any conclusive data on the effect of temperature on flexing. The results seemed to suggest that the effect was very small on the side of lowered resistance to flexing with increase of temperature.

Dispersion of the Carbon Black.—It has been suggested that this factor, dispersion, is the most important. If dispersion is important for resistance to abrasion, and also resistance to flexing, it would be expected that correlation would exist. If Table VIII be compared with Table XI, definite correlation will be observed.

As indicated, there are a great number of factors involved in flexing but in spite of this a high abrasion loss is accompanied by a high flexing index and *vice versa*. Notable exceptions in linseed oil and magnesium linolenate are explained by the softness of the samples.

Study of Dispersion by Means of the Microscope.—The results so far recorded agree with the hypothesis that good dispersion gives good abrasion resistance, and good flexing resistance. It is necessary, however, to study dispersion itself, and not any properties supposed to be dependent thereon.

Of the microscopic methods available, four may be mentioned: (i) examination of a small pellet pressed between glass slides (Grenquist, *Ind. Eng. Chem.*, **20**, 1073 (1928)); (ii) dissolving in solution, spreading on glass slides, allowing to dry, and examining the deposit; (iii) cutting sections from the cured specimen for examination, and (iv) curing specimen up to ebonite, polishing and observing under microscope with vertical illumination.

The latter method described by Roninger (*Ind. Eng. Chem. (Anal. Ed.)*, **5**, 251 (1933)) had the advantage that it was possible to study dispersion as it actually was, without destroying the structure, in uncured or cured stocks. In brief, it consisted in curing the specimen in a bath of sulfur for 24 to 36 hours at 135° to 140° C., cleaning, polishing successively with emery, emery flour, crocus, and rouge powders. Examination was made under the microscope with vertical illumination. Photographs were taken with a panchromatic half-tone plate. The black appears as bright specks or areas on a less brilliant background. No successful method of etching the surface has been discovered. It is to be understood that any carbon black not visible was dispersed so finely as to be unresolved at the particular magnification (40 diameters).

Factors Influencing Dispersion.—The factors influencing dispersion of carbon black in rubber appear to be: the softener present; the plasticity of rubber when addition of carbon black is made; the order of addition of carbon black and softener; the amount of milling after addition of the carbon black; the nature of the black, and of other fillers present.

The effect of the nature of the carbon black has not been studied, as only one black was used throughout the investigation. Also most of the work on dispersion

was done on mixes containing only rubber and carbon black and no other fillers. It has been stated (*Grenquist, loc. cit.; Rev. gén. caoutchouc*, 7, 17 (1930)) that zinc oxide is definitely antagonistic to carbon black in mixing, and further that carbon black tends to flocculate or agglomerate round the sulfur crystal. This point has not been investigated.

In the study of dispersion the most outstanding differences were those caused by the presence of a softener. In the experiment, a quantity of rubber was taken with the softener (4 per cent) added, and 10 per cent quantities of carbon black were milled in to a total of 50 per cent on the initial weight of rubber. A sample for the study of dispersion was removed after each 10 per cent of black had been added.

The conclusion concerning softeners as dispersing agents is, that other factors being inoperative, good dispersion will result in good abrasion and good flexing resistance. The evidence presented here has been for a series of fatty acids and salts, when a good correlation between abrasion and flexing has been observed. As far as the evidence goes, the factor determining these properties is dispersion.

It is not claimed that dispersion alone determines resistance to abrasion and flexing, for the choice of accelerator, antioxidant, cure and so on, have effects, but these points are outside the purview of this paper.

Discussion

In Tables IV and V are given the softening action data, while Table VI gives the melting points of the acids and salts used as softeners, and to which may be added the melting points of the aliphatic alcohol at 48° C. and paraffin wax at 52° C.

From a comparison of the figures in the tables, the first fact that emerges is that a definite action of a physico-chemical nature takes place; otherwise there can be no accounting for the high softening action of substances with melting points of 100° C. and over. The melting point bears no direct relation to the softening action. It is only possible to say that substances of high melting point tend to have little softening action, possibly because of the difficulty of dispersing them in rubber, but liquids do not necessarily give high values, though they mix with, and are absorbed by the rubber.

In the second place, as the alcohol and acid groups are better than the straight aliphatic hydrocarbon, the OH group is important. Further, the presence of barium in place of hydrogen reduces the action to a fraction of that of the acid.

Thirdly, it may be remarked that zinc and magnesium salts have a certain solubility in rubber whether due to some linkage with the natural non-rubber components or the rubber itself.

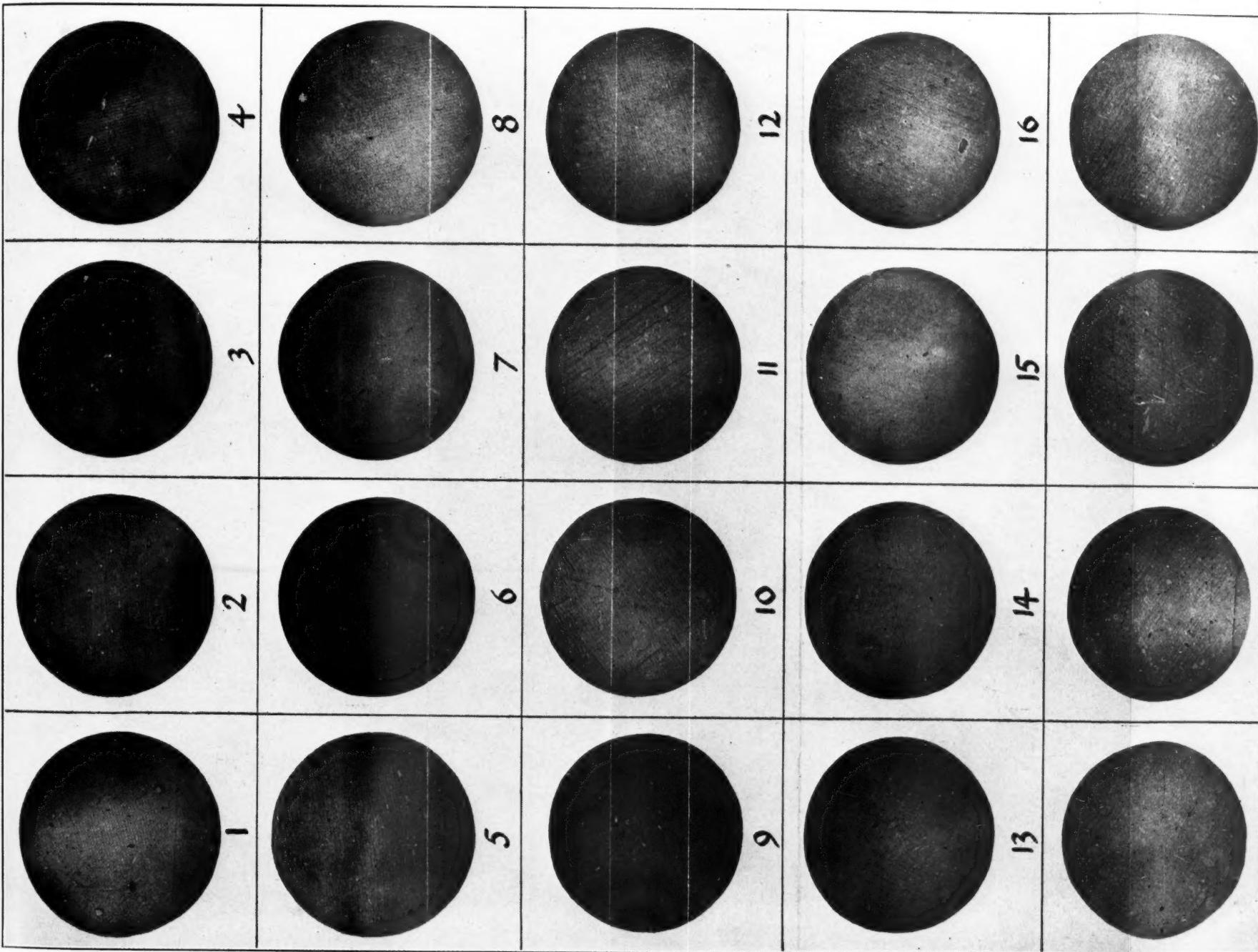
It should be noted that linoleic and linolenic acids and salts were of very similar behavior, due no doubt to the difficulty of obtaining pure products.

In suggesting a theoretical explanation of the data obtained the following facts are significant.

(a) Zinc and magnesium salts follow each other in effect, the zinc salt giving a higher softening figure than the magnesium salt. The apparent inertness of barium salts suggests that they may be neglected, the barium having rendered ineffective the OH group, and raised the melting point of the compound.

(b) There is an increase in softening action from laurie (C12) to stearic (C18) in the case of the acid, but a decrease in the case of the zinc and magnesium salts. The introduction of one double bond, that is, from stearic acid to oleic acid, gave a marked drop in softening action.

(c) There is a rise in softening action from oleic to linolenic in the case of the acids, but a fall in the case of the salts. The introduction of the OH group into



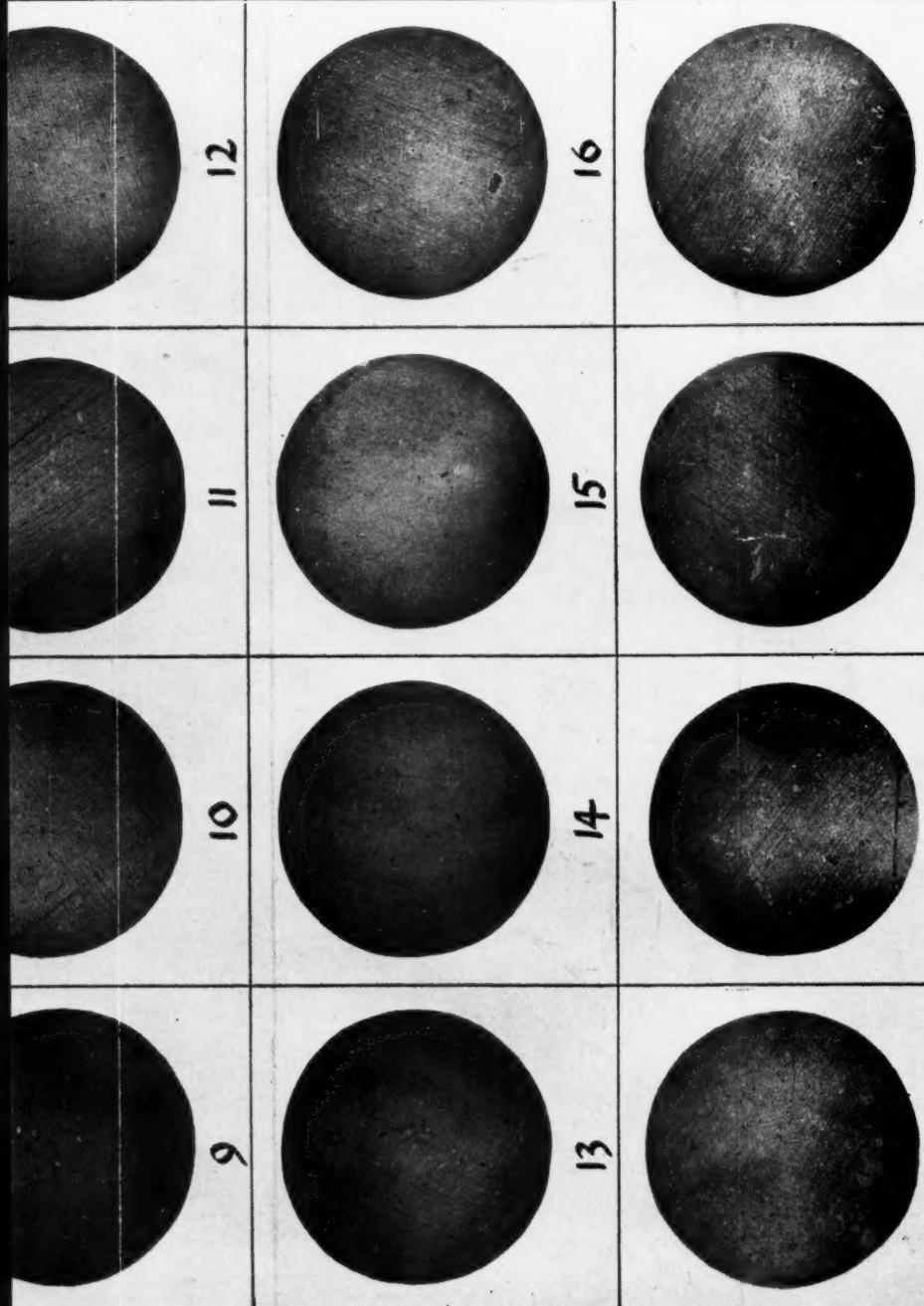
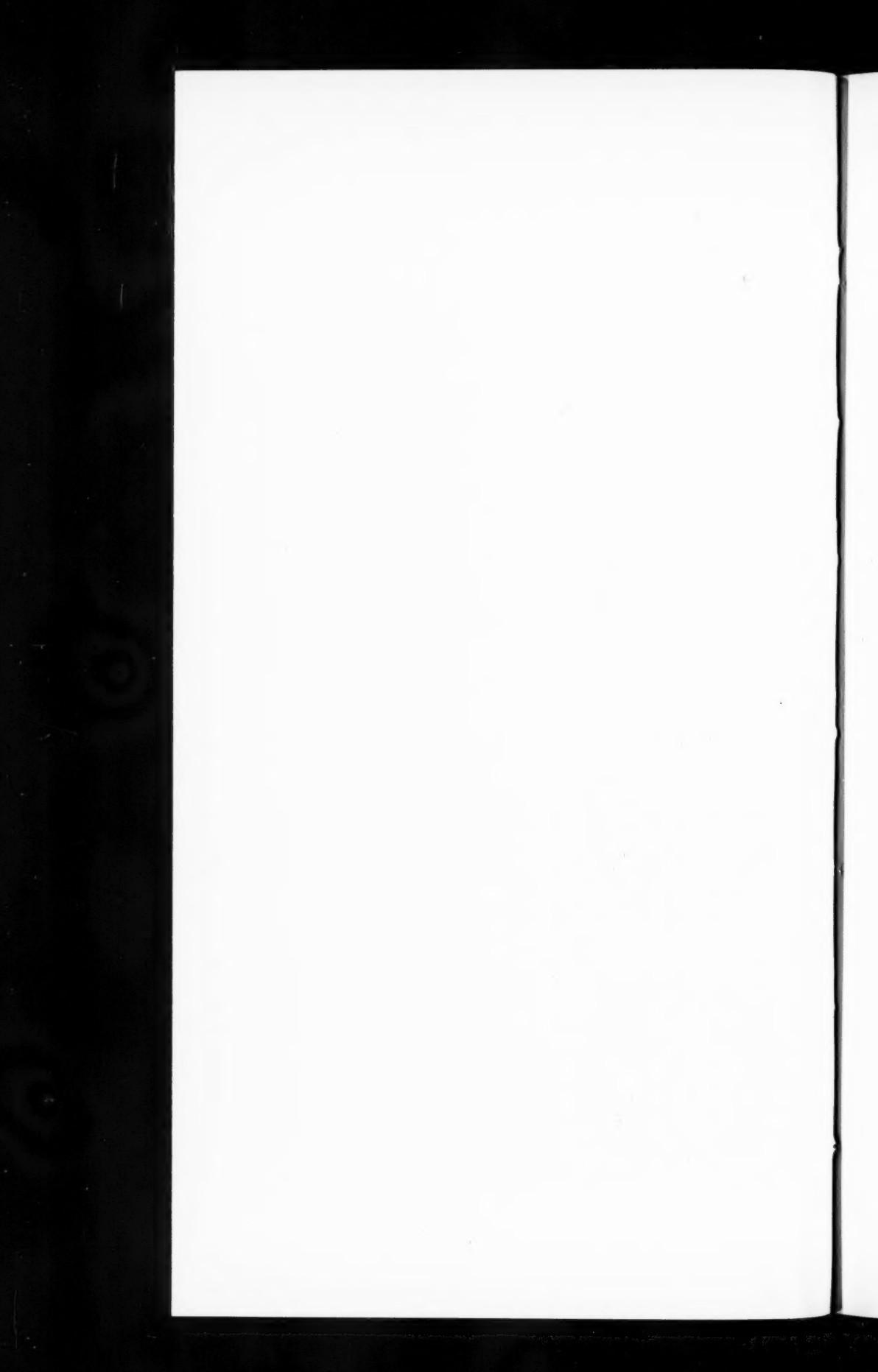


Figure 5





oleic to give ricinoleic produced a reduction of softening action, except in the case of the acid.

(d) The acids, alcohol, and paraffin, have a greater tendency to bloom than the salts of the acids.

The purpose and action of a softener is to separate the molecules, micelles, or aggregates, and to maintain the separation, so that they can slip freely over one another. This effect is presumably accomplished by a film of the softener being formed between the particles. Then the following factors are of importance.

Stability of the Film of the Softener.—This is required to be high. The higher the melting point of the substance, the higher the stability of the film will be.

Adhesion of Film to Rubber.—A certain adhesion is essential, otherwise the film would not spread. An unsaturated substance will show a higher adhesion than a saturated one, and the zinc and magnesium salts apparently have a higher adhesion than the acid, as indicated by the tendency of the latter to bloom.

Rate of Spread of Film.—This needs to be high, otherwise the rubber molecules would aggregate before a permanent separation could be effected. Rate of spread is inversely proportional to molecular weight, but is likely to be reduced when adhesion between the rubber and compound is great.

Size of the Molecule of Softener.—Large molecules will effect a greater softening action due to greater surface covered, and separation obtained. On the other hand, a large molecule will not enter a small opening so readily.

Consideration of the above data in the light of these factors suggests that the lauric to stearic acid figures are explained by an increased stability of film, and an increase of molecule size. The drop from stearic to oleic acid (the *cis*-isomer) is due to a shortening of the effective length of the molecule, and a greater adhesion of the film to rubber. From oleic to linolenic acid an increase in effective length, and an increase in stability of the film, will account for the improvement. The factors of adhesion of the organic chain to the rubber, and the rate of spread, are assumed to be of minor importance in these cases.

In the case of the salts, however, the effective molecule length is greater, the adhesion of the film to the rubber is undoubtedly increased, and so also is the stability of the film. From these two latter factors one would expect the salts to be more effective than the acids. The chief exceptions are zinc stearate, and zinc palmitate. To explain these anomalies it is suggested that the rate of spread is low, due to a high adhesion to the rubber surface and high molecular weight, and further, that the molecules having become unduly large are unable to enter the openings between the molecules. In the case of zinc oleate, and zinc laurate, the molecule is shorter, and so the rate of spread will be greater.

In linking up the acid and salt data, with that of the aliphatic alcohol, and paraffins, no information is available of the behavior of the end groups.

As regards the mechanism of softening itself, no definite explanation can be put forward at present, but the problem seems to be linked with that of mastication. Mastication on the rolls involves a progressive reduction in hardness (as measured by plasticity or viscosity) with the time on the rolls. The rate of softening is very considerably reduced in the absence of oxygen (Cotton, *Trans. Inst. Rubber Ind.*, **6**, 487 (1931)). On allowing the rubber to stand, the process is reversed to a certain extent, and a hardening or stiffening takes place.

A highly active filler, such as carbon black, milled into the rubber reduces the softness still further if plasticity or viscosity measurements are made as soon as the rubber leaves the mill, but on allowing the carbon black mix to stand, a large recovery, or in fact, a set-up takes place to give a rubber of comparatively extreme

hardness. This hard rubber can again be plasticized on the mill, though this is a slower process than the plasticizing of raw rubber (containing no carbon black).

The effect of softeners is to increase the plasticizing rate on the mill, and the softening action has been expressed as minutes of mastication time saved under the standard procedure employed.

In the experiments, a rubber containing carbon black was used as being more suitable for work on softeners, both in their action as softeners and dispersing agents.

From the experiments it appears that once the softener is added, mastication proceeds at a normal rate; that is, the mastication-time curves for rubbers softened by a softener and by mastication are the same, after the same plasticity has been reached. Increase of softness is supposedly due to decreased adhesion, or to a loosening of the bonds between the molecules or particles. It is still open to doubt, however, whether the greatest factor is the breaking of inter-molecular linkages or inter-micellar bonds. By breaking of inter-molecular linkages is implied the shortening of the chain of isoprene molecules, supposed to comprise the rubber molecule. By breaking of inter-micellar bonds is implied the separation of the bundles or swarms of these chains. It has been suggested that because mastication requires oxygen, oxidation plays a part in the process. There is evidence that large quantities of gas are dissolved by rubber, so it is possible that oxygen is a softener in the same way as, say, stearic acid is a softener. The mastication process then becomes the mixing of oxygen into rubber, or a case of gas peptization as Auer has suggested (*Trans. Inst. Rubber Ind.*, 4, 507 (1929)). There is evidence that oxidized rubber, such as that produced by the Ungar-Schidrowitz process, has a softening action on raw rubber. Stearic acid might have an inter-micellar action, but hardly an inter-molecular action, neither is it an oxygen carrier. It can be extracted from the rubber mix; in the same way placing a sheet of masticated rubber in a vacuum desiccator reveals the presence of dissolved gas. There is still, however, the energy required to produce mastication to be borne in mind and the possible effect of any protein structure in the raw rubber. Though mastication is very much lowered in the absence of oxygen, this may be due to the lack of a suitable lubricant to prevent the structure from reforming.

It would be interesting to know if rubber mixes containing carbon black were plasticized in the absence of oxygen, and also if softeners are still capable of softening in the absence of oxygen.

There is undoubtedly a structure or framework in both raw rubber and raw rubber mixes containing carbon black. The action of the softeners is to break this down by some mechanism, at present undiscovered. A similarity of structure in the two cases is instance as justification for using a carbon black-rubber mix for the work on softening.

In addition, the action of these substances as dispersing agents for carbon black in rubber must be borne in mind. In this case it is necessary to disintegrate the black into a fine state of division, and then to surround the microscopic particles so formed by a film, which will prevent subsequent flocculation. There appears to be, however, no definite correlation between dispersing action and softening action. Here, however, the phenomenon is too complex, and too little data are available to permit speculation with theoretical explanation.

APPENDIX 1

Abrasion Resistance at High Temperatures

It has been suggested that the results recorded above can be explained as being

due to the particles of abraded rubber adhering to the specimen which has become tacky, due to the rise of temperature. Some attempt has been made to elucidate this point.

If the reduction in abrasion loss with rise of temperature were due to a tackiness developing, it is surprising that such a small rise of temperature as from, say, 15° C. to 25° C. should give a marked and easily detectable difference. It is hardly conceivable that rubber is tackier at 25° C. than at 15° C. In the second place the brush would assist the removal of the particles, and thirdly, the specimen and abrasive wheel being inclined at an angle to one another, the particles would rapidly work to one edge and leave the specimen.

It has been observed that the abraded particles vary in character from coarse shreds to an exceedingly fine dust. Experiments on mixes yielding particles of all these types have given the same result, and the drop in abrasion loss for a given temperature change bears no definite relation to the character of the abraded particles. It would be expected that the shred-like particles would have more tendency to tackiness and adhesion to the rubber surface than the fine dust, and yet this was not reflected in the results.

The following experiment was carried out using two specimens (M and N) of a black mix of the type that gave, on abrading, a fine dust, which definitely tended to clog the abrasive wheel. Both samples were first given their preliminary run of 2000 revolutions, and were then run for 1000 revolutions as below, and the losses determined.

Specimen	Against Abrasive Wheel	Temperature C.	Loss
M	Clean	75-80	0.734
N	Uncleaned	75-80	0.745
M	Clean	75-80	0.748
N	Uncleaned	Room	1.35
M	Clean	Room	1.30

It seems definite that any effects due to clogging of the abrasive wheel are small in comparison with the large drop of 40 to 50 per cent in abrasive loss due to temperature effects.

APPENDIX 2

Note Concerning Previous Published Work

Burbridge's paper (*Trans. Inst. Rubber Ind.*, 1, 429 (1926)) provides a useful summary of the position at the date of publication. Zimmerman and Cooper (*Ind. Eng. Chem.*, 20, 812 (1928)) published work on softeners and anti-softeners, and quantitative data are given for the softening action based on plasticity determinations with a Williams' instrument of a few softeners, including stearic acid, pine tar, mineral rubber, and cottonseed oil.

De France and Krantz (*Ind. Eng. Chem.*, 23, 824 (1931)) compared the value of pine tar, mineral rubber, and stearic acid in tread stocks. They concluded that a minimum of softener was desirable for high abrasion resistance, if consistent with good factory processing.

Some quantitative data on the relative softening action of various substances is given in a recent paper by Crawford (*Ind. Eng. Chem.*, 26, 931 (1934)).

Grenquist (*loc. cit.*), in a paper on the dispersion of pigments in rubber, concludes that fatty acids prevent agglomeration and flocculation, but that zinc oxide and carbon black are definitely antagonistic in mixing and give rise to flocks.

The effect of a fatty acid, with and without zinc oxide, in accelerator activation is referred to by Dinsmore (*Ind. Eng. Chem.*, **21**, 1722 (1929)) and Fuller (*ibid.*, 723). Zinc oxide needs to be rendered soluble, by means of a fatty acid, for full activation in the case of mercaptobenzthiazole and similar accelerators.

Davey (*J. Soc. Chem. Ind.*, **49**, 338T (1930)) maintains that the function of the fatty acid is not to provide a soluble zinc salt (Whitby and Evans, *J. Soc. Chem. Ind.*, **47**, 122T (1928)) but to prevent flocculation of the oxide, and so increase the surface available for reaction with the accelerator. In a more recent paper by Depew (*Ind. Eng. Chem.*, **24**, 565 (1932)), the dispersion theory is rejected, and further evidence presented to prove that the zinc soap is the activator.

Blake (*Ind. Eng. Chem.*, **21**, 718 (1929)) has concluded that 30 volumes of carbon black can be properly dispersed in 100 of rubber by means of 1.95 per cent of stearic acid. From work on the heat of wetting he proves that, when the black is dispersed in the rubber, the fatty acid wets the filler and not the rubber.

Grenquist (*Rev. gén. caoutchouc*, **7**, 17 (1930)) describes a poor method of mixing carbon black and zinc oxide together, showing poor dispersion at first, improving with milling and cutting, and then becoming worse due to higher plasticity and consequent flocculation. Morris (*Ind. Eng. Chem.*, **24**, 584 (1932)) describes a method for determining the solubility of various substances in rubber.

Summary

1. A method is outlined for the investigation of softeners in rubber compounding; their softening action, their effect on the tensile strength abrasion and flexing properties in a carbon-black tread stock, and their effect on the dispersion of carbon black.
2. The method is applied to the study of a series of fatty acids, their zinc, magnesium, barium salts, and glycerides.
3. Some results are given of the change of abrasion resistance with temperature.
4. A theory of softening action is suggested.

Acknowledgments

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Theory and Application of the Parallel-Plate Plastimeter

Part 2

J. R. Scott

Explanation of Symbols

c	= consistency of material (reciprocal of mobility)
f	= friction or yield value of material, <i>i. e.</i> , a critical shearing stress below which no continuous shear takes place
n	= exponent in the general stress-flow relationship, Equation 1
V	= volume of disc of material under test
θ	= thickness of disc
R	= radius of disc
r	= distance of any point in the disc from its axis
y	= height of any point above the mid-plane of the disc; see Fig. 3
$Y_1 Y_2$	= heights (above mid-plane) of lower and upper boundaries respectively of sheared zone; see Fig. 3.
p	= pressure at the point r, y
v	= rate of horizontal flow of material at the point r, y
θ_L	= limiting thickness, <i>i. e.</i> , thickness below which the disc cannot be compressed by a given force, however long it acts
x	= θ/θ_L
t	= time
D	= $-d\theta/dt$ (<i>Note:</i> Since $d\theta/dt$ is negative, D is positive)
$\log D'$	= ordinate of point on the $\log D - \log \theta$ curve referred to point of intersection of its asymptotes as origin
P	= compressive force on disc
k	= slope of boundaries of sheared zone at or near limiting thickness (k equals $\pi R^2 f/P$)
X	= function of x ; see Equation 6
Z	= function of n and x ; see Equation 15.

I. Introduction

In Part I (*Trans. Inst. Rubber Ind.*, 7, 169 (1931)) a mathematical investigation was made into the behavior, in the parallel-plate plastimeter, of viscous and plastic materials possessing various types of stress-flow relationship. The following generalized form of this relationship was adopted as a basis:

$$A = \left(\frac{F - f}{c} \right)^n \quad (1)$$

where A is the rate of shear under the action of a shearing stress F . The following particular cases were considered: (i) viscous material ($f = 0$; $n = 1$); (ii) quasi-viscous material ($f = 0$; n is greater than 1); (iii) plastic material (f is finite; $n = 1$).

In dealing with the flow of a plastic material when compressed between parallel plates, the basic principle adopted was that the shearing stress is greatest at the surfaces of the plates and diminishes to zero in the plane midway between them; see Fig. 1. There is thus a central zone (shaded in the figure) in which the shearing stress is less than f , and hence no continuous shear takes place. (The reason why the thickness of this zone varies over the disc need not be discussed here; see

Part I, *loc. cit.*) These conditions are analogous to those obtaining in the flow of a plastic material through a tube, where the shearing stress diminishes from a maximum at the walls to zero at the axis, the center of the tube being occupied by an unsheared cylindrical plug of material (concentric with the tube) which moves forward bodily (de Waele, *Kolloid-Z.*, 38, 27 (1926); Bingham, "Fluidity and Plasticity," New York, 1922, Chap. VIII).

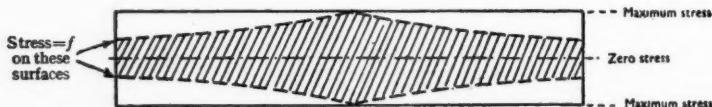


Figure 1—Cross-Section of Disc of Material between Plates

As the thickness of the disc decreases, owing to the outward flow, the unsheared zone becomes thicker at the expense of the sheared (unshaded) zones until the latter disappear, at which stage the limiting thickness is reached and flow ceases.

Since, the theory of the parallel-plate plastimeter was developed on the above basis, it has been shown (Peek, *J. Rheology*, 3, 345 (1932); Nádai, "Plasticity," New York, 1931) that flow does not occur as shown in Fig. 1. The basic principle governing such flow, stated in the words of Peek, is that "for flow to take place, surfaces under a tangential stress f must extend from one free surface of the body to another." Now the tangential stress along any surface making an angle b with the horizontal is $S \sin b \cos b$, where S is the vertical stress (pressure) on the material. Hence the greatest tangential stress occurs along the diagonal surfaces represented in cross-section by the continuous lines AB and CD (see Fig. 2), where $\sin b \cos b$ has its greatest value (assuming b to be small). Consequently, just before the limiting thickness is reached, when the sheared zones are on the point of disappear-

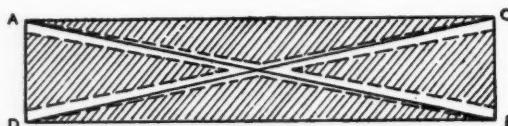


Figure 2—Cross-Section of Disc of Material between Plates (Peek)

ing, these zones must be distributed along the surfaces AB and CD. When the thickness is somewhat greater than the limiting thickness, shear will occur in zones of finite thickness bounded by surfaces such as those shown by the broken lines in Fig. 2. The unsheared zones will thus be of the form shown by the shaded portions of this figure, not as in Fig. 1. On this basis Peek proceeds as follows: consider an annulus of cross-section $dr \times dx$ and radius r , situated in the sheared zone (see Fig. 3); then

$$(y - Y_1) \frac{dp}{dr} = c \frac{dv}{dy} \quad (2)$$

where dv/dy is the rate of shear, and dp/dr the difference of pressure between the inner and outer faces of the annulus. Integration gives an expression for v . By then integrating v with respect to y (taking into account the facts that $v = 0$ when $y = Y_2$, and that when y is less than Y_1 , the value of v is the same as when $y = Y_1$) an expression is obtained for the volume of material flowing outwards across a

cylindrical surface concentric with the disc and of radius r (AA in Fig. 3) in a time-interval dt . As this volume is represented also by the expression $-2\pi r \cdot d\theta$, where $d\theta =$ change in thickness of disc in time dt (the negative sign is inserted because $d\theta$ is negative), these two expressions can be equated, which leads to the following:

$$\frac{3rc}{2} \cdot \frac{d\theta}{dt} = \frac{dp}{dr} (Y_2 - Y_1)^2 (2Y_2 + Y_1) \quad (3)$$

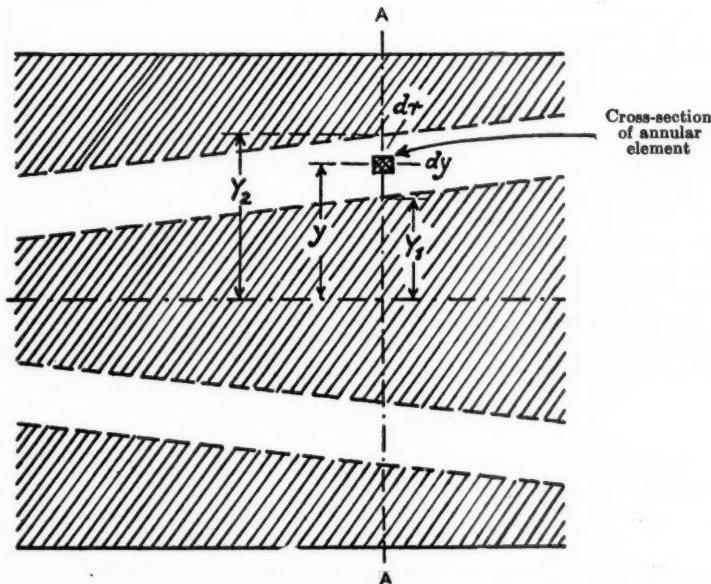


Figure 3—Unsheared Zones Shaded; Sheared Zones Unshaded

In Equation 9 of Peek's paper, the numerical factor $3/2$ is misprinted $2/3$.

On the assumption, which is approximately true for thicknesses not much greater than the limiting thickness, that the boundaries of each sheared zone (broken lines in Fig. 3) are straight and parallel, Peek, finally obtains the following:

$$P = \frac{4\pi cR^4 D(9 - M)}{27\theta(\theta - 2kR)^2} \quad (4)$$

$$\text{where } M = \sum_{N=2}^{N=\infty} \frac{(-kR)^{N-2}(kR - \theta)}{N\theta^{N-1}} \left\{ \frac{9}{2} - \frac{3N + 5 + (-1)^N 2^{N+2}}{(N+1)(N+2)} \right\}$$

The limiting thickness θ_L is given by the formula:

$$f = \frac{\pi^{1/2} P \theta_L^{5/2}}{2V^{1/2}} \quad (5)$$

In formula 4 of Peek's paper the $\pi^{1/2}$ is misprinted as π . The previous investigation described in Part I, and based on the principle illustrated in Fig. 1, gave an expression similar to Equation 5 above but with $3/2$ as the numerical constant instead of $1/2$.

Peek (*loc. cit.*) proceeds to consider an approximate form of Equation 4 obtained by ignoring the summation M and compares the result with experimental data. (Attention may be drawn to a misprint in this paper, p. 361, line 4: $2Rk = h_0$ should read $2Rk < h_0$).

The objects of the investigation described in the present paper were:

(i) To see whether some convenient method could be devised for comparing experimental data with the exact form of Peek's solution as given by Equation 4, instead of having to resort to the approximation used by Peek. It was shown in Part I that in the case of the solution based on the principle illustrated in Fig. 1, the shape of the curve obtained by plotting $\log D$ against $\log \theta$ is independent of the experimental conditions (P and V) and the plastic constants of the material (c and f), and that this fact leads to a simple method of determining whether experimental data agree with the theoretical equation, and, if so, of deducing the plastic constants. It was therefore of interest to see whether the same method could be applied to the solution represented by Equation 4.

(ii) If, as proved to be the case, the simple method just referred to could be applied to Equation 4, it was desired to compare the $\log D - \log \theta$ curve deduced from this equation with that deduced in Part I, to determine to what extent the conclusions there drawn were in error.

(iii) To see whether Peek's method would lead to a convenient solution for the case represented by the general stress-flow relationship, Equation 1, as this had proved impossible by the method used in Part I.

II. The $\log D - \log \theta$ Curve

Following the method adopted in Part I, θ is put equal to $x\theta_L$; substituting for θ_L from equation 5 then gives:

$$\theta = 2^{1/4}xf^2/V^{1/4}/\pi^{1/4}P^{1/4}$$

In Equation 4, R is now put equal to $(V/\pi\theta)^{1/2}$. By substituting the above expression for θ and rearranging, the equation becomes:

$$D = \frac{27f^2V(x^{1/2}-1)^2}{cP(9-X)} \quad (6)$$

$$\text{where } X = \sum_{N=2}^{N=\infty} \frac{(x^{-1/2}-1)}{N(-2x^{1/2})^{N-1}} \left\{ \frac{9}{2} - \frac{3N+5+(-1)^N 2^{N+2}}{(N+1)(N+2)} \right\}$$

From this

$$\log D = \log \frac{27f^2V}{cP} + \log \frac{(x^{1/2}-1)^2}{9-X} \quad (7)$$

Now c , f , V , and P are constants in any one experiment and therefore do not affect the shape of the curve obtained by plotting $\log D$ against $\log x$ but only its position. The shape is determined solely by the second term on the right-hand side of Equation 7; this is purely a function of x , or, since $x = \theta/\theta_L$ and θ_L is a constant in any one experiment, purely a function of θ . It follows that the shape of the $\log D - \log \theta$ curve is independent of c , f , V , and P , that is, of the plastic constants of the material and of the experimental conditions, as was found to be the case with the curve deduced by the earlier method in Part I.

The simple method of comparing experimental data with the theoretical curve, described in Part I, can therefore be used also with the more accurate theoretical curve deduced by Peek's method. The data for plotting this new theoretical curve,

and the coördinates of the point of intersection of its asymptotes, are given in the following Section.

III. Comparison with Curve Obtained by Previous Method

The $\log D - \log \theta$ curve, like that deduced by the earlier method, has two asymptotes:

(i) a vertical asymptote:

$$\log \theta = \log \theta_L = \frac{1}{5} \log \left(\frac{4f^2V^3}{\pi P^2} \right) \quad (8)$$

(ii) an asymptote with an upward slope (from left to right) of 5, represented by the equation:

$$\log D = 5 \log \theta + \log \left(\frac{2\pi P}{3cV^2} \right) \quad (9)$$

The coördinates of the point of intersection of the asymptotes are:

$$\left[\frac{1}{5} \log \left(\frac{4f^2V^3}{\pi P^2} \right), \log \left(\frac{8f^2V}{3cP} \right) \right]$$

It is convenient to take this point as the origin and the vertical asymptote as the vertical axis. The equation to the curve referred to these coördinates is:

$$\log D' = \log \frac{81(x^{5/2} - 1)^2}{8(9 - X)} \quad (10)$$

where $\log D'$ is the ordinate and $\log x$ the abscissa of a point on the curve. As $\log x = \log \theta - \log \theta_L$, and $\log \theta$ and $\log \theta_L$ are the abscissae of points on the original curve and on the vertical asymptote, respectively, $\log x$ is clearly the abscissa of a point on the curve referred to the asymptote as axis.

The corresponding equation deduced by the previous method in Part I is:

$$\log D' = \log \left(x^5 - \frac{3}{2}x^{4/2} + \frac{1}{2}x^{-5/2} \right) \quad (11)$$

The values of $\log D'$ corresponding to various values of x , as given by equations 10 and 11, are shown in Table I and the curves plotted from these values in Fig. 4 (A = old curve, B = new curve).

TABLE I

x	Log x	Log D' (Eqn. 10)	Log D' (Eqn. 11)
1.093	0.0388	2.843	2.922
1.176	0.0704	1.441	1.514
1.319	0.1204	0.035	0.097
1.552	0.1908	0.627	0.671
1.741	0.2408	0.973	1.004
1.904	0.2796	1.219	1.244
2.178	0.3380	1.568	1.585
2.512	0.4000	1.918	1.930

It will be seen that the two curves are very similar, the main difference being that the new one, Equation 10, lies a little further away from the asymptotes. To show more clearly the close resemblance in shape, as distinct from position, the new curve is also shown redrawn in a slightly different position (broken line). The new curve is seen to have merely a trifle less curvature than the old.

It is thus evident that the conclusions drawn in Part I concerning the plastic properties of rubber stocks cannot be seriously altered by the substitution of the new curve for the old one. The comparison of experimental curves with the new theoretical curve is discussed again at the end of Section IV.

IV. Case of the General Stress-Flow Relationship

By using a modification of Peek's method, a solution can be obtained in the case of the general stress-flow relationship represented by Equation 1.

The method follows, in its initial stages, that used by Peek and outlined in Section I above. In the general case Equation 2 becomes:

$$(y - Y_1)^n \left(-\frac{dp}{dr} \right)^n = -c^n \cdot \frac{dy}{dv} \quad (12)$$

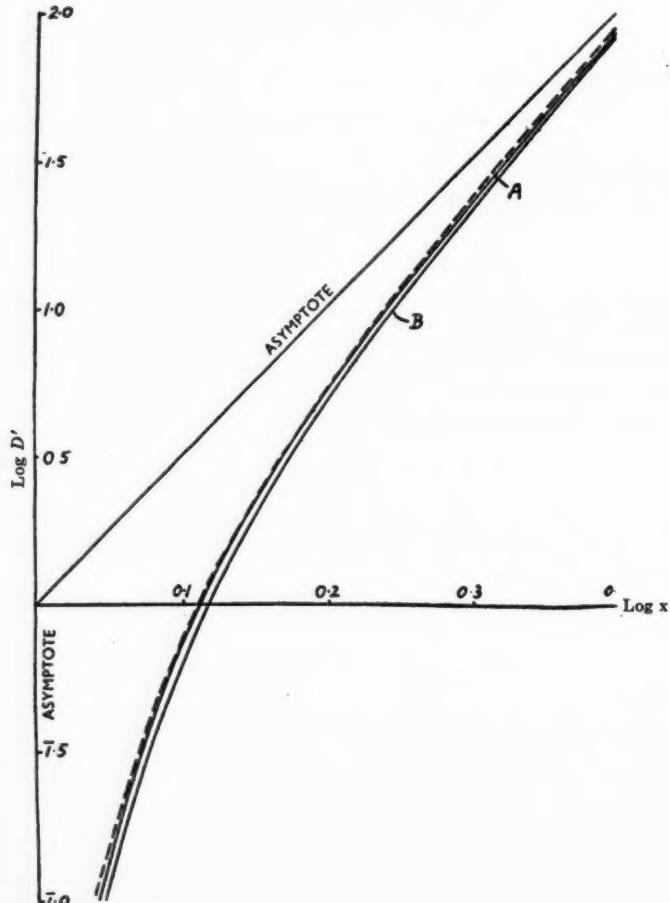


Figure 4— $\log D'$ — $\log x$ Curves (A = Equation 11; B = Equation 10).

dp/dr is a negative quantity because the pressure decreases from the center to the edge of the disc; dv/dy also is negative because the rate of flow decreases from the

mid-plane to the top and bottom surfaces. Integration of (12) under the same conditions as before gives the following analog of Equation 3:

$$-\frac{(n+2)(n+1)rc^n}{4} \cdot \frac{d\theta}{dt} = \left(-\frac{dp}{dr} \right)^n (Y_2 - Y_1)^{n+1} (Y_1 + Y_2 + nY_2) \quad (13)$$

It is assumed, as before, that the boundaries of each sheared zone (broken lines in Figs. 2 and 3) are straight and parallel, so that we may write:

$$\begin{aligned} Y_1 &= kr \\ Y_2 &= 1/2T - k(R - r) \end{aligned}$$

By using these substitutions Equation 13 may be re-written:

$$-\frac{dp}{dr} = cr^{1/n} \left[\frac{2^{n-1}(n+1)(n+2)D}{(\theta - 2Rk)^{n+1}} \right]^{1/n} \left[\frac{(n+1)\theta}{2} + k[(n+2)r - (n+1)R] \right]^{-1/n} \quad (14)$$

The expression raised to the power $-1/n$ is then expanded by the binomial theorem to the required number of terms (4 is sufficient, as the series is rapidly convergent). By integrating with respect to r (introducing the condition that $p = 0$ when $r = R$) an expression is obtained for p .

Now the total force P on the disc must equal the integral of p over the whole disc, i.e., the integral of $2\pi pr dr$ between $r = 0$ and $r = R$. By thus integrating the expression obtained for p and equating to P we obtain, after rearrangement, an expression for D in terms of P, c, θ, R, k , and n .

At or very near the limiting thickness the slope k of the boundaries of the sheared zone equals $\pi R^2 f/P$; as a first approximation it may be assumed, as is done by Peck, that k has the same value for thicknesses not greatly exceeding the limiting thickness. By substituting this expression for k , then substituting for R in terms of θ and V , and finally substituting $2^{1/4}xf^{3/4}V^{3/4}/\pi^{1/4}P^{3/4}$ for θ (as in Section II above), the following equation is obtained:

$$D = \frac{2(3n+1)^nf^{n+1}V(x^{5/2}-1)^{n+1}}{(n+2)Pn^n c^n Z^n} \quad (15)$$

where Z represents an infinite series of which the first four terms are:

$$\begin{aligned} 1 &- \frac{3n+1}{n(n+1)x^{1/2}} \left[\frac{n+2}{4n+1} - \frac{n+1}{3n+1} \right] + \frac{3n+1}{2n^2(n+1)x^6} \\ &\quad \left[\frac{(n+2)^2}{5n+1} - \frac{2(n+1)(n+2)}{4n+1} + \frac{(n+1)^2}{3n+1} \right] \\ &- \frac{(2n+1)(3n+1)}{6n^3(n+1)^2x^{15/2}} \left[\frac{(n+2)^3}{6n+1} - \frac{3(n+2)^2(n+1)}{5n+1} + \frac{3(n+2)(n+1)^2}{4n+1} - \frac{(n+1)^3}{3n+1} \right] \end{aligned}$$

This equation, analogous to Equation 6 for the particular case where $n = 1$, gives the rate of decrease in thickness (D) in terms of the plastic constants of the material (f, c, n), the load P , the volume of the material V , and the ratio (x) of the thickness θ to the limiting thickness θ_L . By using Equation 5 to give a formula for θ_L , D can be expressed in terms of θ instead of x .

When $n = 1$ Equation 15 becomes identical with Equation 6 (evaluating the first three terms of the summation X), as it should do. Similarly, when $f = 0$ the equation becomes identical with Equation 6 of Part I (*loc. cit.*) deduced directly for a quasi-viscous material (n greater than 1; $f = 0$).

It would be possible without difficulty to obtain a general expression for all the terms in the series represented by Z , but it has not been thought necessary to do this because in practice 4 (or even 3) terms are sufficient to give the value of D with adequate accuracy.

It follows from Equation 15 that the shape of the curve obtained by plotting $\log D$ against $\log \theta$ or $\log x$ is independent of the plastic constants of the material or the experimental conditions, as has already been found for the particular case where $n = 1$.

Proceeding as in Section III it is found that the $\log D - \log \theta$ curve has two asymptotes:

(i) vertical asymptote represented by Equation 8;

(ii) asymptote with a slope of $(5n + 5)/2$, represented by the equation:

$$\log D = \frac{5n + 5}{2} \log \theta + \log \frac{(3n + 1)^n \pi^{(n+1)/2} P^n}{2^n n^n (n + 2) V^{(3n+1)/2} c^n} \quad (16)$$

The intersection of the asymptotes is the point:

$$\left[\frac{1}{5} \log \left(\frac{4f^2 V^2}{\pi P^2} \right), \log \left(\frac{2(3n + 1)^n f^{n+1} V}{n^n (n + 2) c^n P} \right) \right] \quad (16a)$$

Taking this point as origin and the vertical asymptote as the vertical axis, the equation for the $\log D - \log \theta$ curve referred to these coördinates is:

$$\log D' = \log \frac{(x^{5/2} - 1)^{n+1}}{Z^n} \quad (17)$$

The values of $\log D'$ corresponding to various values of n and x are given in Table II. The values for $n = 1$ should, of course, be identical with those given in Table I under "Eqn. 10"; they are given again in Table II to show the agreement between the results obtained by the two methods, which serves as a check on the accuracy of the working.

TABLE II

x	Log x	Log D'				
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
1.093	0.0388	2.848	2.194	3.567	4.950	4.337
1.176	0.0704	1.445	1.099	2.777	2.464	2.154
1.319	0.1204	0.036	0.003	1.988	1.977	1.972
1.552	0.1908	0.627	0.907	1.197	1.492	1.789
1.741	0.2408	0.974	1.434	1.903	2.375	2.851
1.904	0.2796	1.220	1.809	2.404	3.003	3.613
2.178	0.3380	1.567	2.336	3.110	3.886	4.663
2.512	0.4000	1.918	2.864	3.815	4.768	5.722
2.874	0.4584	2.235	3.343	4.455	5.567	6.680

The curves of $\log D'$ plotted against $\log x$, for $n = 1, 2, 3, 4$, and 5, are shown in Fig. 5. By comparing these curves with an experimental $\log D - \log \theta$ curve it is possible to see whether the latter coincides with the theoretical one for any integral value of n , or for intermediate values if the corresponding curves are plotted. If agreement is found, the values of f and c can be calculated from the coördinates, on the experimental graph, of the point of intersection of the asymptotes, using the formulae (16a) given above for these coördinates. This method is similar to that described in Part I (*loc. cit.*) for the particular case where $n = 1$.

In Part I it was stated that many unvulcanized rubber stocks gave $\log D - \log \theta$ curves that agreed, within the limits of experimental error, with the theoretical

curve there deduced for the case of $n = 1$, while the others gave curves apparently corresponding to values of n greater than 1, though this latter point could not be tested exactly because the shapes of the curves for these values were not known.

In view of the close resemblance between the two curves for $n = 1$ deduced by the previous method and by the more accurate method described above (Equations 10 and 11, respectively), it would be expected that those experimental results previously found to fit the theoretical curve would fit equally well the new and more accurate curve. This is found to be the case, except that a few experimental curves now appear to correspond to values of n slightly less than 1. All the results that previously appeared to correspond to values of n greater than 1 are now found to fit,

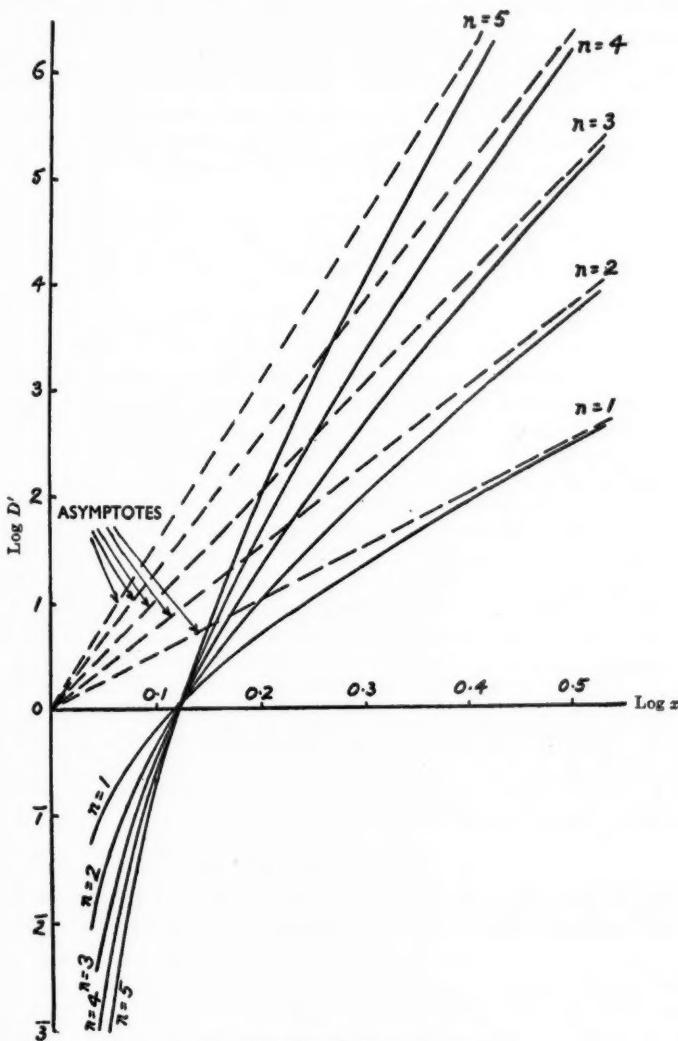


Figure 5— $\log D'$ — $\log x$ curves

within the limits of experimental error, the curves for various values of n between 1 and 2 (curves for various intermediate values were plotted for this purpose). The results of the examination of experimental curves are not given here in detail because these curves are not considered sufficiently accurate to warrant a lengthy discussion in relation to the composition and treatment of the stock. It may be concluded, however, that to a first approximation unvulcanized rubber stocks at 90° C. show stress-flow relationships represented by forms of Equation 1 with various values of n .

V. Summary and Conclusion

In Part I (*loc. cit.*) the behavior of a plastic material in the parallel-plate (Williams) plastimeter was studied, and an expression was deduced showing how the rate of decrease in thickness of the sample during compression depends on the volume of the sample, its plastic properties, the compressive load, and the thickness itself. Subsequently, observations were published which showed that the basic principle adopted in this study was incorrect in certain particulars. Peek (*loc. cit.*), using these observations as a basis, deduced a new expression for the rate of decrease in thickness, though this is too complex for convenient practical use, except in an approximate simplified form.

It has now been shown that the expression deduced in Part I, in spite of the inaccurate basis used, is sufficiently near to the truth to render substantially correct the conclusions there stated concerning the plastic properties of unvulcanized rubber stocks.

By adopting the more accurate basis used by Peek, moreover, expressions for the rate of decrease in thickness can be deduced for materials showing more complex types of plastic flow than that considered in Part I or by Peek; this had proved impossible by the method previously used. The expression obtained by Peek for the simple type of plastic flow, as well as those now deduced for the more complex types, can be expressed in a form that furnishes a simple and rapid method of examining and analyzing experimental results.

As a result of the work described in this paper, it is thus possible to determine, from results obtained with the parallel-plate plastimeter, whether or not a material such as unvulcanized rubber stock exhibits any of the types of plastic flow represented in the general form by Equation 1, and, if so, to find the values of the plastic constants of the material. The procedure is similar to that described in Part I, and consists simply in comparing, by superposition, a set of standard curves drawn on transparent paper with the curve plotted from experimental data.

This further development of the method of studying plastic properties by means of the parallel-plate plastimeter should greatly increase its utility as an instrument of research. It has not yet been possible to apply the new method to a systematic study of rubber stocks, but from an examination of existing data it appears that these stocks, tested at 90° C., agree approximately with various forms of the generalized plastic flow equation already referred to.

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The Problem of the Evaluation of Reclaimed Rubber by Analytical Methods

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Since the problem of the reclaiming of rubber and the increased use of reclaimed rubber in the rubber and cable industries, even in Germany, has again become of importance, interest in methods for the evaluation of reclaimed rubber has naturally increased.

It has been recognized in the past that chemical tests can give only a general idea of the approximate composition of a reclaimed rubber, while they show little or nothing about its mechanical properties. Accordingly in most countries, only the most important chemical determinations have been carried out, such as the acetone extract, ash content and sometimes the combined sulfur, while in the case of black reclaimed rubbers, carbon black and sometimes the cellulose present in the rubber, which are determined by difference, are also included. When carbon black is present in high percentage, as is particularly true of modern tire treads, the results of the determination of the quantity of rubber substance are much too high.

Therefore the Rubber Control Bureau in Berlin has justifiably required direct information on the carbon black and cellulose in black live-steam reclaimed rubber. The ash and carbon black contents are evident also in the specific gravity of the reclaimed rubber. The specific gravity is most reliably determined with a vulcanized sample or with very thin, smooth sheets by means of the suspension method in zinc chloride solution of suitable concentration.

The proportion of the acetone extract, which in good reclaimed rubber should not exceed 10-12 per cent, gives only an uncertain idea of the physical properties of the rubber substance. A better means of evaluating the physical properties is afforded by the vulcanization test, which is carried out in various ways in different countries.

Thus in the United States, reclaimed rubber is mixed with 5 per cent of sulfur, in Germany with 3 per cent of sulfur and 0.5 per cent of diphenylguanidine, whereas in England 2 per cent of sulfur, 2 per cent of zinc oxide, and 0.5 per cent of diphenylguanidine, based on the quantity of reclaimed rubber, are usually added. Even vulcanization is carried out at different temperatures. After times of cure which are in most cases 15, 20, and 30 minutes, the tensile strength and elongation are ordinarily measured, and less frequently the resistance to abrasion, the resistance to bending and the aging properties.

It seems desirable that internationally recognized chemical and physical methods of testing reclaimed rubber should be adopted in the countries which are the more important producers and consumers of reclaimed rubber, as is the case already with many other important products, such as leather.

A vulcanization test is time-consuming, and requires a large sample, though it is of the greatest importance to the manufacturer of reclaimed rubber for controlling the uniformity of his various batches. In the case of the consumer of reclaimed

rubber, the most important question is to know the behavior of the reclaimed rubber on the mill, its ease of mixing with raw rubber, its ease of swelling and solubility in ordinary commercial rubber solvents particularly in benzine hydrocarbons, (for making cements). As is well known, these properties depend to a great extent upon the degree of "devulcanization" or the degree of "reversion" of the reclaimed rubber.

If the inexact information obtained on the important components of a reclaimed rubber by the difference method is unsatisfactory, it is in addition a difficult problem to obtain any reliable information on the physical properties in cases where only a small sample is available. It would therefore be of the utmost value to have a simple, and at the same time a fairly certain analytical method for the technical evaluation of a reclaimed rubber.

Recently Zilchert¹ pointed out the importance of the determination of the chloroform extract of reclaimed rubber, which makes it possible on the one hand to decide upon the method used in reclaiming (*e. g.*, steam or alkali process) and on the other hand to obtain an idea of the quality of the product itself. The idea of using the proportion of chloroform extract for evaluating reclaimed rubber is by no means a new one. Thus in 1928, Lindmayer² described a long series of experiments on this subject, from which he drew a few conclusions on the method of preparing reclaimed rubber. According to Lindmayer, the magnitude of the chloroform extract (in percentage based on the rubber) is an index of the so-called "degree of devulcanization" and, based on theoretical considerations, he came to the conclusion that the chloroform extract would have to be approximately 48 per cent of the rubber content of the reclaimed rubber, and this he designated as 100 per cent devulcanization. In practice this is not approached, and only in the case of a French reclaimed rubber (probably a solvent reclaim, according to Lindmayer) did he find evidence of a degree of devulcanization of 95 per cent.

By devulcanization Lindmayer does not assume the original idea of "desulfurization," but rather the rupture of the rubber chain molecules, which are combined during vulcanization by means of sulfur bridges, into fragments richer in sulfur and fragments containing (theoretically) no sulfur. The magnitude of this latter chloroform-soluble part, expressed in percentage of the total vulcanized rubber substance, Lindmayer designates as the degree of devulcanization.

In the same journal, Loewen³ discussed this work of Lindmayer critically, especially his theoretical conclusions, and also emphasized the importance of an exhaustive investigation of the whole complicated problem which had been initiated by Lindmayer.

Prompted chiefly by practical necessity, I have during recent months studied the chloroform extracts of a series of foreign and domestic reclaimed rubbers from the best known sources and of the best quality in relation to the physical tests of the reclaims after vulcanization. The remaining part of the present paper will report these results briefly, and perhaps they will serve to clarify this problem further.

The investigation included domestic and foreign live steam and alkali reclaimed rubbers. In the case of foreign reclaims the investigation was concerned throughout with quality brands from the leading reclaim factories, which had been supplied in the spring of the past year.

The reclaimed rubbers in the form of thin sheets were first extracted with acetone in a Soxhlet for 8 hours on a steam bath, and were then extracted for the same time with chloroform. In Tables I and II, in addition to the acetone extracts and the chloroform extracts mentioned, the usual important analytical data from a series

of live-steam and alkali reclaims (treads and inner tubes) are summarized. The chloroform extracts of light and red reclaims are always yellowish brown, those of black reclaims are generally reddish to dark brown, which is partly due to the small residue of bitumin in the latter. With live-steam reclaims containing carbon black, an 8-hour extraction with chloroform is in general sufficient. On the contrary, after another 8-hour extraction, alkali reclaims and especially inner tube reclaims still yield considerable quantities of chloroform-soluble substances, as is evident from the values in Table III.

TABLE I
ANALYSIS OF LIVE STEAM-RECLAIMED RUBBERS

Raw Material Used Number Method of Treatment	Auto Tire Treads			Inner Tubes			Air Bags 7 6% Plas- ticizer 8 Hrs. at 183° C.	Unknown 8 Un- known known
	1 4% Plas- ticizer 6 Hrs.	2 3% Plasticizer 8 Hrs.	3 183° C. 10 Hrs.	4 3% Plasticizer 6 Hrs.	5 183° C. 8 Hrs.	6 Un- known		
	at 175° C.							
(a) Sp. gravity	1.18	1.18	1.17	1.12	1.12	1.10	1.35	...
(b) Acetone extract	12.8	10	9.6	8.6	8.8	9.7	7.4	19.4*
(c) Chloroform ex- tract	9.8	11	12.4	10.4	10.6	16	18.6	9.0
(d) Ash	17	17	18.3	20	20	20	35.0	33.3
(e) Carbon black	12	12	12	8 (Approx.)
(f) Cellulose	6	6	6
(g) Insoluble vulcan- ized rubber	42.4	44	41.7	64	60.6	54	39.0	28 (Approx.)
(h) Total vulcanized rubber	52.2	55	54.1	71.4	71.2	70	57.6	39 (Approx.)

* Including 14.7% mineral oil, probably added as a plasticizing agent.

TABLE II
ANALYSES OF ALKALI-RECLAIMED RUBBERS

Raw Material Used Source Number Method of Treatment	Auto Tire Treads			Inner Tubes			American 7 Unknown	English 8 Unknown
	1 Without Plasticizer 183° C. 10 Hours	2 3% Plasticizer 183° C. 24 Hrs.	3 Un- known	4 Un- known	5 Un- known	6 Un- known		
	183° C. 10 Hours	24 Hrs.						
(a) Specific gravity	1.2	1.2	1.16	1.16	1.17	1.25	1.13	1.17
(b) Acetone extract	7.5	8.8	12	11.5	11.4	10.2	10.0	11.4
(c) Chloroform ext.	11.8	12.6	11.6	18.4	16.6	14.0	24.5	18.3
(d) Ash	21	21	17	18.0	20.6	25	23.5	26.7
(e) Carbon black	16	16	10	12	8	8	5.0	...
(f) Insoluble vulcan- ized rubber	43	41.6	49.4	40	40	45.1	37.0	43.6
(g) Total vulcanized rubber	50.5	54.2	61.0	58.4	56.6	59.8	61.5	61.9

Nevertheless in the present investigation an 8 hours' chloroform extraction was used as a basis, since even after this length of time characteristic differences both between the individual types of reclaimed rubber and between the various representatives of the same class were evident. With a longer chloroform extraction, the results become complicated by a peptization of the difficultly soluble portion, as is the case with raw rubber. The variations in the values of the chloroform extracts, which can be reproduced within an error of ± 1 per cent, with the same type

of reclaimed rubber for the same time of extraction, are shown in Table IV. From this it is seen that the values of the chloroform extracts, based on a total rubber substance in the reclaim of 100, varied in the case of the live-steam reclaimed rubbers between 15 and 23, with one exception. The essentially higher value of the chloroform extract of the gray air-bag reclaimed rubber is explained by the fact that in the case of this reclaimed rubber there is an extensive "reversion" or "de-vulcanization" of the rubber substance in the original material as a result of the repeated heating. The values of the chloroform extract of the domestic alkali reclaimed rubbers which were reclaimed at 183° C. were between 20 and 23, and are approximately the same as those of the live-steam reclaimed tread rubber, whereas the corresponding values for the foreign alkali-reclaimed rubbers were between 30 and 40 with one exception. These higher chloroform extracts of the latter reclaimed rubbers are unquestionably attributable to the generally higher temperatures of reclaiming during their production. On the other hand, the length of time of the reclaiming process at the same temperature has no essential influence on the chloroform extract (see No. 3, Table II).

TABLE III
RELATION OF THE QUANTITY OF THE CHLOROFORM EXTRACT TO THE TIME OF EXTRACTION

Time of Extraction in Hours	Auto Tire Treads		Inner Tubes		Alkali Reclaim No. 8 in Table II
	Live Steam Reclaim No. 1 in Table I		Alkali Reclaim No. 5 in Table II		
	Quantity of Extract Based on Reclaim	Quantity of Extract Based on Rubber	Quantity of Extract Based on Reclaim	Quantity of Extract Based on Rubber	Quantity of Extract Based on Reclaim
8	9.8	19	16.6	29	18.3
10	11.0	21	19.9	35	20.0
					42

TABLE IV
RELATION BETWEEN THE QUANTITY OF THE CHLOROFORM EXTRACT AND THE QUALITY OF VULCANIZATES OF LIVE STEAM- AND ALKALI-RECLAIMED RUBBERS

A. Live Steam Reclaims from Table I

Number	1	2	3	4	5	6	7	8
(a) Chloroform extract in % of total rubber	19	20	23	14.5	15	23	32	23
(b) Tensile strength (kg. per sq. cm.)	40	60	60	23	23	45	72 (68)	32
(c) Percentage elongation at rupture	250	300	320	370	380	340	520 (500)	250
(d) Quality index	110	180	192	85	87	153	375 (340)	80

B. Alkali Reclaims from Table II

Number	1	2	3	4	5	6	7	8
(a) Chloroform extract in % of total rubber	22	23	19	31	29	23	40	30
(b) Tensile product (kg. per sq. cm.)	55	70	54	75	76	45	110	54
(c) Percentage elongation at rupture	310	320	290	470	500	400	580	580
(d) Quality index	170	224	157	352	380	180	638	313

Parallel with these chloroform-extract determinations, vulcanization tests of simple sulfur-accelerator mixtures of these reclaimed rubbers were also carried out. The mixtures containing 3 per cent sulfur and 0.5 per cent diphenylguanidine were prepared under conditions as nearly the same as possible, and were vulcanized in a press at 145° C. for 15, 20, and 30 minutes. From the vulcanized sheets, which were about 2 millimeters thick, samples were die-cut in all cases in the same direction of milling for the tensile strength tests. The tensile strengths and the elongations of the samples vulcanized to the optimum degree, which was in most cases 20 minutes, are shown in Table IV under the corresponding chloroform ex-

tracts. The mathematical product of the optimum tensile strength and elongation divided by 100 was chosen as a product (P) for comparison of quality. Even a superficial comparison of these P values with the corresponding chloroform extracts of the raw reclaimed rubbers shows an unmistakable correlation between the two properties. This relation is still more evident in the graphic representation of the relation.

In so far as any regularity may exist, as judged by the relatively few measurements, it is evident in the course of the curves shown in the diagram. A trend of this character in the curve is to be expected, because the chloroform extracts must approach a limiting value which, in the present case where the vulcanization coefficients are 4 to 5 and the extraction periods are 8 to 16 hours, would have a value around 50, which is in agreement with the data of Lindmayer, though not with his theoretical considerations.

Of interest also is the fact that the chloroform extract- P curve of live-steam reclaimed rubber lies to the left of the otherwise identical curve for the alkali reclaimed rubber, so that for the same chloroform extracts of the raw reclaims the P values of the vulcanized live-steam reclaimed rubbers are somewhat lower than those of alkali reclaims. This is to be explained by the fact that the "nerve" of the portion of the reclaimed rubber which can be vulcanized again, and is represented by the chloroform extract of the reclaim, has suffered more than in the alkali reclaim, in spite of the generally higher temperature of vulcanization of the latter. This is true to a much greater extent with products which have been made with the aid of large proportions of plasticizing agents (see Table IV, A, No. 8). In this way a new experimental proof is offered on the one hand of the fact that long, practical experience has shown that alkali reclaims have superior physical properties to those of live-steam reclaims, and on the other hand of the importance of the chloroform extract as a criterion of the physical properties, at least for alkali reclaims.

That the chloroform-soluble raw rubber-like portions above all else in a reclaimed rubber play an essential part in revulcanization is evident from the fact that the chloroform extracts of reclaims decrease to an extraordinary extent upon vulcanization, as is shown in Table V. During vulcanization with 3 per cent sulfur and 0.5 per cent diphenylguanidine, the chloroform extracts are reduced to one-fourth to one-fifth of their corresponding values in the raw reclaim. A similar observation has already been made independently by Lindmayer (*loc. cit.*).

On the other hand, his theoretical considerations do not appear to be sound, because reclaiming splits the vulcanized molecule into a portion practically free of sulfur and a portion richer in sulfur. As sulfur determinations of chloroform extracts have shown, the latter still contains anywhere from small to large quantities of combined sulfur (see Table VI). Of further interest is the fact that the

TABLE V
INFLUENCE OF REVULCANIZATION ON THE QUANTITY OF THE CHLOROFORM EXTRACT
OF VULCANIZED RECLAIMS

	Reclaimed Inner Tubes (Live-Steam Process)			Reclaimed Treads (Live-Steam)		
	With 3% Sulfur + 5% Diphenylguanidine	With 3% Sulfur + 5% Di-phenyl-guanidine				
Unvulcanized	20 Min. at 145° C.	25 Min. at 145° C.	Unvulcanized	20 Min. at 145° C.	Unvulcanized	20 Min. at 145° C.
Acetone extract	8.2	8.0	...	8.8	9.2	9.9
Chloroform extract	11.2	2.6	2.0	10.6	2.3	8.6
						9.0
						2.2

TABLE VI

COMBINED SULFUR IN THE CHLOROFORM EXTRACT OF ALKALI-RECLAIMED RUBBER
EXTRACTED WITH ACETONE

No. in Table II	Reclaimed Treads				Reclaimed Inner Tubes	
	4	5	6	7	8	No. 6 in Table I
Time of extraction (in hours)	8	16	8	16	8	8
% combined sulfur in chloroform ext.	0.94	1.47	1.27	0.49	0.59	1.55
C ₆ H ₆ molecules per S atom	48	38	36	98	81	32
% combined sulfur in residue	2.6
C ₆ H ₆ molecules per S atom	10

reclaims with the lowest sulfur contents in the chloroform extracts have at the same time the highest values for these extracts, and as has been shown they also possess the highest *P* values for the particular vulcanizates. Of course there do not seem to be such clear relations between the sulfur content of the chloroform extracts and the physical properties of the reclaims as there are between the chloroform extracts and the *P* values. However, it may possibly be that by means of extensive physico-chemical tests of the chloroform extracts, still further conclusions along these lines can be reached.

The following explanation may perhaps account for the complexity of the relations described above. As is well known, raw rubber contains an easily soluble sol component and a more difficultly soluble gel portion. As is also well known, the proportions of these two components can be changed⁴ considerably by long, continued extraction as a result of peptization or by mechanical-thermal pretreatment. Thus, according to Pummerer and Pahl, the extracted sol portion from smoked sheet, treated with boiling ether as the extracting agent for about 100 hours, was approximately 75 per cent, and that from crepe was only about 45 per cent of the total rubber, whereas preliminary acetone extraction of the crepe caused an increase in the sol rubber portion to about the same amount as with smoked sheet. During vulcanization, the sol as well as the gel portion combines with the sulfur chemically, in which form is here immaterial. The rate of combination of sulfur depends above all else upon the rate of vulcanization of the two portions. The difference in the rates of vulcanization between the sol and gel rubber is to be expected from their greatly differing nitrogen content.⁵ In each case rubber-sulfur complexes will be formed, having different degrees of sulfurization (coefficients of vulcanization), and consequently of different solubilities. It may be foreseen that also during reclaiming these complexes will undergo different degrees of reversion or devulcanization. Therefore it is to be assumed that the sol portions having less sulfur will again become more easily soluble than the gel complexes⁶ containing more sulfur. In any case the tough, essentially more highly sulfurized, chloroform-insoluble residue of the reclaim resembles very closely in its physical properties the difficultly soluble gel skeleton of raw rubber.

From this point of view, reclaiming is found to be a more or less extensive, preponderantly colloid-chemical decomposition of the vulcanizate into more easily soluble sol rubber, poor in sulfur, and into more difficultly soluble gel rubber rich in sulfur. That here very complicated relations are involved is already evident from the results of Pummerer and Koch (*loc. cit.*) upon the mutual convertibility of sol and gel rubber in raw rubber. Nevertheless it would be of great theoretical interest, and in view of the economic importance of reclaiming, it would also be of practical interest, to carry out more extensive and systematic investigations leading to a better insight into these problems.

References

- ¹ Zilchert, *Gummi-Ztg.*, **49**, 367 (1935).
- ² Lindmayer, *Kautschuk*, **4**, 278 (1928).
- ³ Loewen, *Kautschuk*, **5**, 61 (1929).
- ⁴ "Handbuch der Kautschukwissenschaft," pp. 205.
- ⁵ *Ibid.*, p. 190.
- ⁶ According to investigations by Smith and Holt (*J. Research Natl. Bur. Standards*, **13**, October, 1931) the difference in the coefficient of vulcanization between sol and gel rubber does not seem to be important. It should not be forgotten that these investigators used purified *Hevea* latex, so that the assumptions just mentioned are not true to the same extent.

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Studies on the Acetone Extraction of Raw Rubber

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I. The Effect of the Time of Heating of the Alcohol Solution on the Determination of the Acid Value of Raw Rubber and Its Acetone Extract

The free fatty acids of the acetone extract of raw rubber were studied by Whitby (*J. Soc. Chem. Ind.*, **42**, 336T (1923); *India-Rubber J.*, **90**, 382 (1925)), Bedford and Winkelmann (*Ind. Eng. Chem.*, **16**, 32 (1923)), Dekker (*India-Rubber J.*, **70**, 815 (1925)), Van Rossem and Dekker (*Ind. Eng. Chem.*, **18**, 1152 (1926)), Bruni and Levi (*Giorn. chim. ind. applicata*, **7**, 447 (1925)); and Buizov (*India-Rubber J.*, **71**, 99 (1926)).

In order to study the change of the free fatty acids during acetone extraction, some conditions necessary for the satisfactory determination of acid value were studied in the present paper. Pale crepe from one shipment was cut into a considerable number of pieces of rectangular shape (about 4 cm. wide and about 8 cm. long). The weight of one sheet was about 1.6-2.0 grams. These sheets were stored in a stoppered bottle made of brown colored glass and filled with nitrogen.

(A) In the first experiment, one sample piece of the rubber mentioned above was placed in a flask, 50 cc. of ethyl alcohol was added, and the flask was heated on a water bath. After heating the flask for a definite time, the acid was titrated with 0.1 N KOH solution, using phenolphthalein as indicator. The number of milligrams of KOH necessary to neutralize the free acids in 1 gram of raw rubber is taken as the acid value of raw rubber and is recorded as the acid value (R).

TABLE I

Sample (G.)	Time of Heating (Min.)	Acid Value (R)
1.7269	10	2.60
1.6760	20	3.01
1.7834	30	2.98
1.6432	40	3.06
1.5828	50	2.83
1.6224	60	2.93

The acid value (R) increased with increasing time of heating, reaching a maximum between 20 minutes and 40 minutes, and after 40 minutes it decreased.

(B) In the second experiment, five sheets of the pale crepe sample previously mentioned were extracted with acetone for 8 hours. The acetone extract was poured into a measuring flask of 250-cc. capacity, and acetone was added up to the

mark. Four lots of 50 cc. of the acetone solution were pipetted out into weighed flasks, the acetone was evaporated off and the flask dried and weighed. Fifty cc. of ethyl alcohol was added to the acetone extract thus obtained and the flask heated on a water bath. The alcohol solution was then titrated with 0.1 N KOH solution, using phenolphthalein as indicator. The number of milligrams of KOH necessary to neutralize the free acids contained in 1 gram of acetone extract is taken as the acid value for the acetone extract and is recorded as acid value (A).

TABLE II
SAMPLE 8.5632 G. (5 SHEETS)

Acetone Extract (G.)	Acetone Extract (%)	Time of Heating (Min.)	Acid Value (A)	Acid Value (R)
0.0624	3.65	Acetone extract dissolved on water bath (3 min.)	98.7	3.60
0.0592	3.46	15	104.1	3.60
0.0592	3.46	30	104.1	3.60
0.0586	3.42	60	100.3	3.44

The acid value (A) was found to be low for the acetone extract not heated and high for the acetone extract heated for 15–30 minutes, and it decreased with 60 minutes of heating.

The above two experiments for the determination of the acid value may be summarized as follows:

(1) For raw rubber: The sample is put into 50 cc. of ethyl alcohol, heated on a water bath for 30 minutes, and titrated with 0.1 N KOH, using phenolphthalein as indicator.

(2) For the acetone extract: Fifty cc. of ethyl alcohol is added to the flask containing the acetone extract, and the flask is heated for 15 minutes on a water bath, after which the solution is titrated with 0.1 N KOH solution, using phenolphthalein as indicator.

II. The Influence of Heating at 100° C. and Storing of the Acetone Extract on Its Acid Value

(A) *The relation between the time of heating the acetone extract at 100° C. and the acid value.*

In the next experiment the acetone extract was dried in a steam oven, and the relation between the time of heating the acetone extract at 100° C. and acid value was studied. Five sheets of the pale crepe sample were extracted with acetone for definite times, *viz.*, 8, 16, and 24 hours, respectively. The acetone extract thus obtained was poured into a measuring flask of 250-cc. capacity, and acetone added to the mark. Four lots of 50 cc. of acetone solution were pipetted into weighed flasks, the acetone was evaporated off and the flasks after drying for 3 minutes in a steam oven were cooled and weighed. The flasks were then heated in a steam oven for varying times, *viz.*, 15, 30, 60, and 120 minutes, cooled and weighed. The acid value was then determined.

(a) Acetone extract obtained from 8 hours' continuous extraction.

TABLE I
SAMPLE 8.6000 G. (5 SHEETS)

Acetone extract (g.) A ₀	0.0562	0.0556	0.0636	0.0610
Acetone extract (%)	3.27	3.23	3.87	3.54
Time of heating (min.)	15	30	60	120
Acetone extract after heating (g.) AT	0.0564	0.0558	0.0634	0.0585
Acetone extract after heating (%)	3.28	3.25	3.69	3.40
0.1 N KOH (cc.)	1.05	1.0	1.05	1.0
Acid value (A)	104.7	100.7	92.5	91.8
Acid value (AT)	104.2	100.3	92.7	95.7
AT/A ₀ (%)	100.36	100.36	99.53	95.91
Acid value (R)	3.42	3.26	3.42	3.26

(b) Acetone extract obtained from 16 hours' continuous extraction.

TABLE II
SAMPLE 9.1006 G. (5 SHEETS)

Acetone extract (g.) A ₀	0.0610	0.0638	0.0616	0.0600
Acetone extract (%)	3.35	3.52	3.38	3.30
Time of heating (min.)	15	30	60	120
Acetone extract after heating (g.) AT	0.0622	0.0652	0.0610	0.0600
Acetone extract after heating (%)	3.42	3.58	3.35	3.30
0.1 N KOH (cc.)	1.1	1.15	1.1	1.1
Acid value (A)	101.0	101.0	100.0	102.7
Acid value (AT)	99.6	99.0	101.0	102.7
AT/A ₀ (%)	101.97	102.19	99.03	100.00
Acid value (R)	3.39	3.54	3.39	3.39

(c) Acetone extract obtained from 24 hours' continuous extraction.

TABLE III
SAMPLE 9.1186 G. (5 SHEETS)

Acetone extract (g.) A ₀	0.0612	0.0640	0.0622	0.0638
Acetone extract (%)	3.35	3.51	3.41	3.50
Time of heating (min.)	15	30	60	120
Acetone extract after heating (g.) AT	0.0620	0.0644	0.0622	0.0628
Acetone extract after heating (%)	3.40	3.50	3.38	3.45
Color of acetone extract after heating	pale	pale	pale	
	yellow	yellow	brown	brown
0.1 N KOH (cc.)	1.1	1.1	1.05	1.05
Acid value (A)	100.7	96.3	94.5	92.2
Acid value (AT)	99.3	95.7	95.5	93.6
AT/A ₀ (%)	101.31	100.63	100.00	98.45
Acid value (R)	3.39	3.39	3.23	3.23

The acid value, which is expressed relative to the acetone extract after heating, is recorded as the acid value (AT). This value (AT) decreased gradually for the 8-hour acetone extract, showed almost no change for the 16-hour acetone extract, and decreased gradually for the 24-hour extract. Generally speaking, the acetone extract had a tendency to increase in weight, possibly owing to oxidation, and it then decreased because of partial evaporation of the acids.

(B) *The relation between storage of the acetone extract and its acid value.*

(a) Storing of the acetone extract in a desiccator. Flasks containing the acetone extract from 8 hours' continuous extraction were kept in a desiccator filled with calcium chloride at room temperature (not in the dark) and the acid value was determined after 1, 2, and 3 days.

TABLE IV
SAMPLE 7.9200 G. (5 SHEETS)

Acetone extract (g.)	0.0471	0.0521	0.0460	0.0486
Acetone extract (%)	2.97	3.29	2.91	3.06
Days extract stored	0	1	3	5
Odor of acetone extract	no change	slightly foul odor	aged foul odor	aged foul odor
Acetone extract after storing (g.)	0.0471	0.0521	0.0530	0.0466
Acetone extract after storing (%)	2.97	3.29	3.34	2.94
0.1 N KOH (cc.)	0.9	0.95	0.9	0.75
Acid value (A)	107.0	102.1	109.5	86.4
Acid value (AT)	107.0	102.1	95.1	90.1
AT/A ₀ (%)	100.0	100.0	114.8	96.1
Acid value (R)	3.18	3.36	3.18	2.65

A part of the acids volatilized after 1 day, and subsequently acids formed possibly from oxidation. Later a further amount of the acids volatilized.

(b) Storage of the acetone solution of the extract. Four stoppered flasks, each containing 50 cc. of the acetone solution of the extract, were stored in a dark place at room temperature. After storing, the acetone was evaporated, the flasks were dried and weighed, and the acid value was determined.

TABLE V
SAMPLE 8.1926 G. (5 SHEETS)

Days extract stored	0	1	3	5
Acetone extract after storing (g.)	0.0515	0.0562	0.0540	0.0480
Acetone extract after storing (%)	3.15	3.43	3.30	2.93
0.1 N KOH (cc.)	0.95	1.0	0.95	0.8
Acid value (A)	103.3	108.8	103.3	87.0
Acid value (AT)	103.3	99.7	98.5	92.2
AT/A ₀ (%)	100.0	108.9	104.8	93.1
Acid value (R)	3.25	3.41	3.37	2.74

The acetone extract increased in weight after 1 day's storing, possibly owing to the oxidation, but after this it decreased. The acid value expressed relative to the acetone extract after storing is recorded as the acid value (AT). This value (AT) decreased with the time of storage.

From the results obtained in the above experiments, the conditions to be followed for the determination of the acid value are as follows: The acetone is evaporated from the acetone extract soon after completion of the extraction, the residue is dried for less than 15 minutes in a steam oven, and the extract is cooled and weighed. Fifty cc. of ethyl alcohol is then added, the flask is heated on a water bath for 15 minutes and the acid is then titrated by 0.1 N KOH solution, using phenolphthalein as indicator.

III. Effect of the Time of Acetone Extraction of Raw Rubber on the Acid Value of the Acetone Extract and of the Acetone-Extracted Residue

In order to extract rubber for long periods, say 16 hours, the extraction may be carried out according to one of the following methods:

(1) The time of extraction is divided into 8 hours. That is to say, the extraction is carried out for 8 hours in the daytime and re-started in the morning of the next day.

(2) The extraction is carried out continuously from the start to the finish without stopping even at night.

(3) The extraction is carried out arbitrarily, making the total time the required period.

In the present paper type method (1) is non-continuous extraction and method (2) is continuous extraction.

(a) *The relation between the time of extraction and the acid value of the acetone extract in non-continuous extraction.*

The sample of pale crepe was extracted for 8 hours in the daytime, the extraction was stopped at the end of the day, and acetone in the extraction cup was lowered into the extraction flask. The sample in the extraction cup was left undisturbed until the start of extraction on the next day. The sample was wet with acetone during this suspension of extraction at night.

TABLE I

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extract (%)	Acid Value (A)	Acid Value (R)
1	1.3906	0.0420	3.02	106.7	3.22
2	1.4400	0.0476	3.31	105.9	3.50
3	1.8016	0.0595	3.31	103.5	3.42
4	1.6638	0.0540	3.25	103.7	3.36
5	1.9061	0.0644	3.39	100.0	3.38
6	1.8420	0.0600	3.26	102.7	3.34
7	1.6934	0.0545	3.22	102.8	3.31
8	1.7264	0.0630	3.65	93.3	3.41
10	1.9447	0.0729	3.75	92.2	3.52
12	2.0008	0.0763	3.82	88.1	3.42
14	1.8700	0.0710	3.80	90.7	3.44
16	1.7668	0.0632	3.57	97.5	3.41
18	1.4904	0.0561	3.76	94.8	3.56
20	1.7200	0.0590	3.43	94.9	3.26
22	1.6856	0.0590	3.50	94.9	3.32
24	1.6664	0.0586	3.52	95.6	3.36

(b) *The relation between the time of extraction and the acid value of the acetone-extracted residue in non-continuous extraction.*

The acetone-extracted residue from the sample extracted in experiment (a) above was placed in a flask containing 50 cc. of ethyl alcohol, and the acid value was then determined as mentioned in Section (I).

TABLE II

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extracted Residue (G.)	Acid Value of Acetone Extracted Residue	Acid Value (R)
1	1.3906	0.0420	1.3486	0	0
2	1.4400	0.0476	1.3924	0	0
3	1.8016	0.0595	1.7421	0.3	0.3
4	1.6638	0.0540	1.6098	0.4	0.3
5	1.9061	0.0644	1.8417	0	0
6	1.8420	0.0600	1.7820	0	0
7	1.6934	0.0545	1.6389	0	0
8	1.7264	0.0630	1.6634	0	0
10	1.9447	0.0729	1.8718	0.3	0.3
12	2.0008	0.0763	1.9245	0	0
14	1.8700	0.0710	1.7990	0.3	0.3
16	1.7668	0.0632	1.7036	0	0
18	1.4904	0.0561	1.4343	0	0
20	1.7200	0.0590	1.6610	0.3	0.3
22	1.6856	0.0590	1.6266	0	0
24	1.6664	0.0586	1.6078	0	0

(c) *The relation between the time of extraction and the acid value of the acetone extract in continuous extraction.*

The results of extraction up to 8 hours are the same as in (a), the figures for the extraction longer than 8 hours being given in the following table:

TABLE III

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extract (%)	Acid Value (A)	Acid Value (R)
10	1.8540	0.0540	2.92	88.0	2.68
12	1.2500	0.0376	3.01	89.4	2.69
14	1.6276	0.0584	3.59	91.1	3.27
16	1.6279	0.0586	3.60	90.8	3.27
18	1.6954	0.0612	3.61	96.1	3.47
20	1.6714	0.0532	3.18	94.7	3.18
22	1.7268	0.0534	3.09	89.2	2.77
24	1.5834	0.0512	3.23	93.0	3.01

(d) *The relation between the time of extraction and the acid value of the acetone-extracted residue in continuous extraction.*

The figures for extractions longer than 8 hours are shown in the following table:

TABLE IV

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extracted Residue (G.)	Acid Value of Acetone Extracted Residue	Acid Value (R)
10	1.8540	0.0540	1.8000	0	0
12	1.2500	0.0376	1.2124	0	0
14	1.6276	0.0584	1.5692	0	0
16	1.6279	0.0586	1.5693	0	0
18	1.6954	0.0612	1.6342	0.2	0.2
20	1.6714	0.0532	1.6182	0.2	0.2
22	1.7268	0.0534	1.6734	0.2	0.2
24	1.5834	0.0512	1.5322	0	0

Summary of Results

In the extraction of pale crepe with acetone, the free fatty acids were almost all removed in 1-2 hours' extraction. The acid value (A) had a tendency to decrease gradually up to 12 hours of extraction, but it increased gradually after 12 hours. The cause of the decrease of the acid value (A) from the start of extraction up to 12 hours is thought to be due to: (1) a gradual increase of non-acid compounds extracted with increased time of extraction, and (2) neutralization of the acids by other compounds, such as esterification. The cause of the increase of acid value (A) after 12 hours is thought to be due to (1) formation of free acids by the decomposition of esters, and (2) formation of acids by oxidation. From the fact that the acid value of the acetone-extracted residue is almost nil even after only 1 hour's extraction, acetone extraction for 1 hour extracted almost all the free acids contained in pale crepe. Therefore the change of acid value of the acetone extract with increase of time of extraction is not due to a change which some other compounds extracted might give, but must be due chiefly to the change in the acetone solution of the extract during extraction. From these results, the free acids are thought not to be adsorbed on the raw rubber nor combined molecularly, but to be dissolved in raw rubber. So far as the change of free acids in the acetone extract is concerned, the acetone extract is very labile. Therefore in storing the acetone ex-

tract, whether it is dried or even in acetone solution, care must be taken not to store it for too long. The acetone extract obtained during very long periods of extraction is believed to have undergone some change.

IV. The Relation between the Time of Saponification and Saponification Value of Raw Rubber and Its Acetone Extract

The determination method of the saponification value of pale crepe and its acetone extract was studied.

(A) *Alcoholic potash for the determination of the saponification value.*

As to the concentrations of the alcoholic potash and of the HCl solution for titration 0.2 N and 0.1 N, respectively, were found to be suitable. The amount of 0.2 N alcohol KOH used for the determination was 20 cc.

(B) *The relation between the time of heating with alcoholic KOH and the saponification value of raw rubber.*

A sample of pale crepe was placed in a flask and 20 cc. of alcoholic KOH was added. After heating for varying times, the solution was titrated with 0.1 N HCl solution, using phenolphthalein as indicator. The number of milligrams of KOH necessary for 1 gram of raw rubber was designated as the saponification value (R), the results being as follows:

TABLE I

Sample (G.)	Time of Saponification (Min.)	0.1 N HCl (Cc.)	Saponification Value (R)
2.1714	30	2.05	5.29
1.8158	60	2.3	7.10
1.9748	90	2.55	7.23
1.8058	120	2.7	8.38
1.8892	150	3.1	9.19
1.3068	180	2.55	10.93

Taking the time of saponification in minutes as abscissa and the saponification value (R) as ordinate, the time-saponification curve is convex up to 60 minutes and concave after this time, there being a point of inflection at 60 minutes. It may be seen from the curve that saponification proceeds gradually to 60 minutes, after which time the rubber, which is now fully expanded, gradually absorbs KOH. Therefore, 60 minutes is considered to be a suitable time of saponification.

(C) *The relation between the time of saponification and the saponification value of the acetone extract.*

(a) Acetone extract from 8 hours' continuous extraction.

Five sheets of the pale crepe sample were taken and extracted continuously with acetone for 8 hours, and the acetone solution of the extract was poured into a measuring flask of 250-cc. capacity. Acetone was then added to the mark. Four lots of 50 cc. were pipetted into weighed flasks, the acetone evaporated off, and the extract dried and weighed. Twenty cc. of alcoholic KOH was added to the acetone extract thus obtained, and the mixture was heated on a water bath for 60 minutes. The excess KOH was titrated back with 0.1 N HCl, using phenolphthalein as indicator. The number of milligrams of KOH necessary to saponify 1 gram of acetone extract is expressed as the saponification value (A).

TABLE II
SAMPLE (5 SHEETS) 7.2808 G.

Acetone extract (g.)	0.0478	0.0508	0.0468	0.0468
Acetone extract (%)	3.28	3.49	3.22	3.22
Time of saponification (min.)	15	30	60	90
0.1 N HCl (cc.)	1.25	1.55	1.5	1.5
Saponification value (A)	146.4	170.9	179.5	179.5
Saponification value (R)	4.81	5.96	5.77	5.77

The heating time for saponification is next considered from the standpoint of change of ester value as follows:

TABLE III

Acid Value (A)	Acid Value (R)	Time of Heating (Min.)	Ester Value (A)	Ester Value (R)
104.1	3.60	15
104.1	3.60	30
100.3	3.44	60

(See Table II in the Previous Paper (1))

Saponification Value (A)	Saponification Value (R)	Time of Heating Min.	Ester Value (A)	Ester Value (R)
164.4	4.81	15	42.3	1.21
170.9	5.96	30	66.8	2.36
179.5	5.77	60	79.2	2.33

(See Table II)

In the above table, the ester value of the acetone extract is recorded as ester value (A) and the ester value of the original raw rubber as ester value (R). It can be seen from the above table that saponification is complete in 60 minutes.

(b) The acetone extract from 16 hours' continuous extraction.

TABLE IV
SAMPLE (5 SHEETS) 7.8200 G.

Acetone extract (g.)	0.0514	0.0536	0.0554	0.0524
Acetone extract (%)	3.29	3.43	3.55	3.35
Time of saponification (min.)	15	30	60	90
0.1 N HCl (cc.)	1.2	1.25	1.35	1.35
Saponification value (A)	130.7	130.6	136.5	144.3
Saponification value (R)	4.29	4.48	4.83	4.83

(c) The acetone extract from 24 hours' continuous extraction.

TABLE V
SAMPLE (5 SHEETS) 8.1377 G.

Acetone extract (g.)	0.0628	0.0602	0.0527	0.0567
Acetone extract (%)	3.86	3.70	3.23	3.49
Time of saponification (min.)	15	30	60	90
0.1 N HCl (cc.)	1.45	1.4	1.4	1.4
Saponification value (A)	129.3	130.2	148.8	138.2
Saponification value (R)	5.00	4.82	4.82	4.82

Summary of Results

(1) For the determination of the saponification value of the acetone extract, 20 cc. 0.2 *N* alcoholic potash is added to the extract and the flask is heated on a water bath for 60 minutes. It is then titrated with 0.1 *N* HCl solution, using phenolphthalein as indicator.

(2) When the saponification values of the acetone extracts of 8, 16, and 24 hours are compared, the saponification value of the 8 hour extract is seen to be high, while those of 16 and 24 hour extracts are low. This indicates (*a*) that the 8 hour extract contains a higher percentage of saponifiable matter than the 16 and 24 hour extracts; (*b*) the quantity of rubber hydrocarbon which is dissolved in the acetone extract increases with increasing time of extraction, and (*c*) the acid value of the acetone extract decreases during the period of extraction from 16 to 24 hours.

(3) Regarding the saponification values (R) of the acetone extracts of 8, 16, and 24 hours, similar remarks may be made as in (2) above.

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Research on Modified Rubbers

Part V. Technological Properties of Chlorinated Rubbers from Latex

P. Schidrowitz

Bloomfield and Farmer, in a paper on "The Preparation of Chlorinated Rubbers from Latex" (*J. Soc. Chem. Ind.*, **53**, 43 (1934); *RUBBER CHEM. AND TECH.*, **7**, 320 (1934)) have described the chief chemical properties of the products prepared by them. The object of the present paper is to describe briefly some characteristics of these products from the technological standpoint.

It will be remembered that, although Bloomfield and Farmer were able to prepare a soluble chlorohydrin from one batch of latex, all other batches yielded insoluble products, although some modification of this insolubility was attained by the addition of serum from the satisfactory latex to those latices which were refractory in this regard. Moreover, the latex which yielded soluble products at first, subsequently no longer did so. Similarly the products from the initially satisfactory latex, at first soluble, underwent a gradual change, becoming less and less soluble. The technical examination of the chlorohydrin from latex therefore proved to be difficult. However, as it was thought possible that a method producing substances of more or less consistent composition and solubility might be later developed, the soluble product referred to was examined from the point of view of ascertaining its suitability as a basis for lacquers, moldings, plastic masses and films.

Direct Moldings

Preliminary work in the laboratory showed that the soluble chlorohydrin could be molded by means of pressure and heat, and subsequently trials were made in a factory producing synthetic resin moldings. The resultant products were inclined to be brittle, and the temperature range within which molding could be carried out and decomposition did not take place was found to be narrow.

In a further set of experiments it was found that the material decomposed and charred completely at about 230° F., and when heated under molding conditions at about 275° F. it decomposed with explosive violence. Finally, moldings were made with stabilized chlorinated latex rubber mixed with various fillers.

Moldings were made at 280° and 300° F., and within this range apparently good moldings were obtained, though the color was rather dark. At this point, in view of the difficulty of obtaining a consistent and satisfactory basis material, the experiments were abandoned.

Plastic Masses

Attempts were also made to gelatinize the material with a view to working along the lines of celluloid manufacture, and in this connection a number of gelatinizing agents, plasticizers and solvents, and combinations of same were tried out. No satisfactory gelatinized product which could be worked on the mill to give a plastic mass was obtainable, crumbly, discreet products always resulting.

Lacquers and Films

It was thought that solutions of the chlorohydrin might be suitable as a rubber lacquer, but though numerous experiments were carried out, no truly satisfactory

products were obtained. A number of trials were also made with the object of producing cast films with and without plasticizers and also admixed with nitrocellulose, but with negative results.

Part Va. Technological Properties of Rubber Oxidation Products

In their paper on "The Oxidation of Rubber with Aqueous Hydrogen Peroxide-Acetic Acid Mixtures" (*J. Soc. Chem. Ind.*, **53**, 121T(1934); RUBBER CHEM. AND TECH., **7**, 454 (1934)). Bloomfield and Farmer have discussed the more important chemical properties of the products obtained by them. Regarded from the technological point of view, these products as a series proved to be distinctly interesting. It is the object of this paper to describe some of the experiments made with a view to ascertaining their practical utility. The products in question are of course not oxides, but hydroxylated and acetylated derivatives obtained by an oxidation process. Where necessary they will be referred to for the sake of simplicity as "product X," where "X" refers to the letter of the alphabet by which the material in question is described in Bloomfield and Farmer's paper.

The products were examined from the point of view of use as films, moldings, and lacquers, and in conjunction with synthetic resins.

Solubility

The solubility of the various products in a number of solvents has been described by Bloomfield and Farmer. In amplification it may here be stated that it was found that product H, for example, was also soluble in tricresyl phosphate and in linseed oil.

Films

In a preliminary series of experiments it was found that a film made from an alcoholic solution of A does not show a high gloss and is rather brittle. Films made from the same product in sextone yielded a high gloss, but were also rather inclined to crack. Films made from B in alcohol showed high gloss, but otherwise were inferior to those made from A. The most promising films were obtained from product H. Cast from alcohol they showed high gloss and flexibility and, made from a solution in sextone, the gloss and flexibility were also found to be good. Sextone, from the point of view of flexibility of the film, was found to be better than alcohol.

A firm of manufacturers to whom samples of the above described products were submitted stated that these materials were most interesting. With regard to H particularly, it was considered that this had excellent possibilities as a protective coating, especially for the electrical industries, and dispersions made from H gave somewhat translucent films which were very flexible.

The opinion was also voiced that H might prove to be superior to existing products as a wrapping material, since it gave films of very low water diffusion. In the course of another series of experiments it was found that films cast from solutions containing tricresyl phosphate, alcohol, and sextone in addition to H, were rather soft and very adhesive, and as a result of further work it appeared likely that this type of H mixing might make a good anchorage medium for other lacquers, for instance, for those derived from chlorinated rubber.

Lacquers

It was also believed, in view of the excellent adhesion of the special films described

above, and having regard to the fact that product H was found compatible with nitrocellulose, that it (H) might find application in nitrocellulose lacquers in place of the synthetic resin usually employed as the anchorage medium. With this end in view a general purpose lacquer of the following composition was made up: 40 g. $\frac{1}{2}$ sec. nitrocellulose; 20 g. product H; 10 g. dibutyl phthalate; 15 cc. amyl acetate; 15 cc. ethyl acetate; 10 cc. sextone B; 15 cc. xylene; 55 cc. toluene; 5 cc. alcohol, and 15 cc. acetone. The results obtained were regarded as promising.

Molding

"Straight" moldings under conditions similar to those used in the manufacture of synthetic resins showed that products B and M yielded transparent glassy substances which were rather brittle but of comparatively good color, M being rather superior to B. Similar experiments with H showed that the moldings were by no means as brittle as those obtained with A, B, or M, and also that H could be molded at a higher temperature than the others. Thus, when molded at 250° F., M gassed badly and stuck to the mold, whereas under the same conditions the behavior of H was much more satisfactory. Mixings made with M and fillers such as wood-flour and whiting, and various plasticizers also yielded a sticky and unsatisfactory gummy mass. It will be seen from what follows that H gave distinctly better, in fact reasonably satisfactory, moldings. It should be noted that M, compared with H, was obtained by oxidation with a reduced amount of acetic acid, and it seems quite likely therefore that, viewed from a molding point of view, M is oxidized far enough to lose its specific rubber properties but not far enough to give the properties of a resin. This view, as has been indicated, was confirmed by making up mixings of H along the general lines of commercial synthetic resin mixings. For example, a mixing consisting of 15 parts H, 8 parts wood-flour, 1 part whiting, and 1.5 parts stearic acid, was mixed on rubber rolls and then molded in the ordinary way at 280-290° F., to form an ash tray. The quality and appearance were quite fair, and it seemed obvious that by varying the mixings, moldings of reasonably good quality could be obtained. From the way in which the surplus was extruded from the join of the mold, H appeared to be an eminently suitable material for injection molding, in the manufacture of which comparatively high-priced materials are used.

The above mixing was therefore tried out in an injection molding press at about 320° F., and it was found that the material behaved very well under these conditions.

Synthetic Resins

A number of experiments were made with a view to ascertaining whether product H could be used in connection with the manufacture of synthetic resins of the bakelite type, and after some experimenting a resin was obtained by boiling the following under reflux and then vacuum-distilling 45 grams of oxide F, 45 grams of phenol, 45 grams of formalin, and 10 cc. of 0.880 ammonia. The result was a clear brittle resin.

The general conclusion from the investigation of the rubber oxidation products dealt with above, was that at a suitable production cost they should be quite useful commercial materials. For certain limited purposes, the production cost would probably be satisfactory even at the present time, but the essential factor as regards their application on a considerable scale is the reduction in the cost of manufacture of peracetic acid. The problem of doing this is a difficult, but I do not think an unsolvable, one.

It is desired cordially to acknowledge the valuable assistance and collaboration of C. A. Redfarn and of M. W. Philpott, by whom the experimental work was carried out.

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Research on Modified Rubbers

Part VII. Expanded Chlorinated Rubber*

P. Schidrowitz and C. A. Redfern

In the course of a research on the properties and applications of chlorinated rubber, some trials in connection with moldings were carried out in an ordinary plunger or positive mold of the type which has been used in molding synthetic resin compositions. It was expected that dense but perhaps comparatively flexible moldings would be obtained, and this indeed is the case under certain conditions, *e. g.*, when the mold is allowed to cool under pressure, and the temperature of molding is relatively low. When, however—as is the practice when molding material of the bakelite type—a comparatively high mold temperature (in the neighborhood of 320–350° F.) was employed, and the pressure released while the mold was still hot, it was observed that a remarkable product was obtained of a light, strong, fibrous, cellular character, many times the size of the mold cavity (British Patent 424,561).

Expanded chlorinated rubber is more readily obtained from certain commercial brands of chlorinated rubbers than from others, or alternatively, the degree of fluffiness or porosity, strength, and so on may vary according to the brand used, other conditions being equal. After a certain amount of experimentation, however, it was found practicable so to modify conditions of molding that the majority of the brands on the market yielded reasonably satisfactory results (see below).

Method of Production

The most elementary method of expanding chlorinated rubber consists substantially in heating the powdered material at a mold temperature range of roughly 320° to 350° F. under pressure, and then opening the mold while the material is still hot. The time of heating will depend on the size of the mold, but in a small mold (see Fig. 1) approximately 2 $\frac{1}{4}$ in. diameter by 1 $\frac{3}{8}$ in. deep, a heating period of 3 minutes at 325° F. was found to be sufficient for the first chlorinated rubber tested, to which we shall refer as *A*.

As the material seemed suitable for extrusion, the next step taken was to have a special mold made, provided with a closable extrusion orifice. The nature of this mold is indicated in Fig. 2.

Finally it was found that the expanded product could be obtained by means of the apparatus used for injection molding, *e. g.*, the chlorinated rubber was introduced into the heated cylinder of the press, and without closing the ejection orifice, pressure was applied by means of the ram, whereby the material extruded through the orifice, and immediately expanded on leaving the latter (cf. Fig. 3).

On a commercial scale it is believed that a plant of the general character indicated diagrammatically in Fig. 4 should be suitable.

In explanation it may be pointed out that, owing to the low heat conductivity of the material, an extrusion mold of the nature indicated in Fig. 2 cannot, owing to the mass of material treated at any given moment, give regular results. This was definitely shown by the improved results obtained with an apparatus of the type

* For Part VI of this series of Papers by G. F. Bloomfield and E. H. Farmer, see *J. S. C. I.*, 54, 125T (1935); *RUBBER CHEM. AND TECH.*, 8, 335 (1935).

illustrated by Fig. 3. That is to say, regular and controlled heating of comparatively small masses of material in any given unit of time is necessary. Having ascertained this fact, it was then found that in order to give regular shape, control of the product was necessary between the extrusion and setting period. By extruding between adjusted plates an improvement was again effected, but owing to the rapid setting of the material and the friction of the plates, jamming of the extruded products between the plates occurred, thus preventing further extrusion. From the preliminary experiments made, it is believed that this difficulty can be overcome by extruding between endless, rotating metal bands, actuated by rollers as indicated in Fig. 4.

In order to obtain a board 12 inches in width, it has been found that the extrusion slit must be approximately one-half of this dimension, namely, 6 inches.

Characteristics of Expanded Product

Structure.—The general structure of the expanded material appears to be that of a network of non-communicating cells, the cell walls showing flow lines. The size of the cells varies according to the degree of expansion. Figure 5 is a sketch of a section examined at a magnification of 92 diameters. This section was taken from the middle of a block of the expanded product. Figure 6 is a sketch (at the same magnification) of a section of the outer skin of the same block.

It will be observed that in the latter case the cell walls are of a more elongated character. When the degree of expansion is comparatively small, a section cut through a block has an appearance similar to that of a light colored wood. When the expansion is high, the apparently fibrous character—the pseudo-fibers being similar in appearance to spun glass—is quite striking, but the fibrous appearance is generally most pronounced on the exterior of the product. The outer layers are perhaps best described as being similar to long-fibered asbestos on the

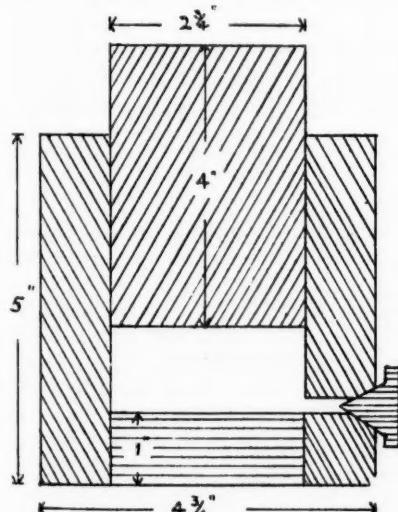


Figure 2

one hand, and the inner portions as mica-like on the other hand. It is noteworthy that even at a high degree of expansion, that is to say, when the apparent specific gravity is less than 0.1 the structure is quite firm, and will resist appreciable pressure without collapsing. Material even of the lightest character can, for example, readily be sawn.

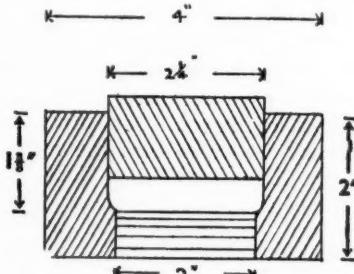


Figure 1

Specific Gravity.—As already indicated, the apparent specific gravity of the material may vary widely, according to the degree and method of expansion, but firm products with an apparent specific gravity as low as 0.087 have been obtained.

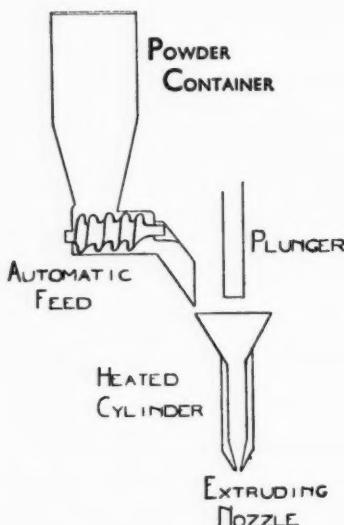


Figure 3

water by submerging completely by means of a sinker, was found (in the case of the expanded product of specific gravity 0.087) to absorb after 24 hours 49.4% and after 48 hours 50.3% of its own weight of water. For practical purposes, therefore,

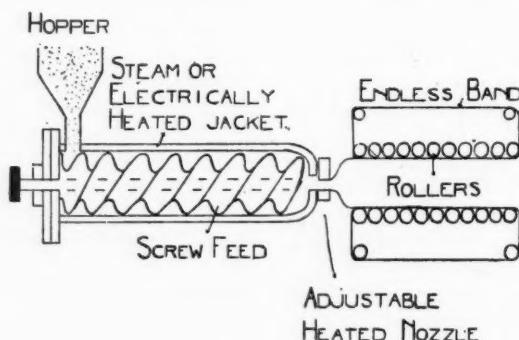


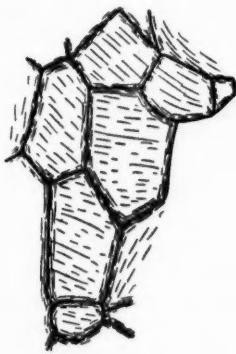
Figure 4

it may be taken that the maximum water absorption of material of the very light type is in the neighborhood of 50% of its weight. That is to say, when completely "water-logged" it still has a great reserve of buoyancy in water, the apparent specific gravity then still being approximately of the order 0.13.

Chemical and Physical Properties.—In view of the fact that it was obviously desirable to ascertain the chemical and/or physical nature of the expansion process,

and having regard also to the variable behavior of the different brands or grades of chlorinated rubbers on the market as regards expansion, an investigation in connection with chemical composition and stability was undertaken. Practically the whole of this work, with the exception of certain data obtained in our own laboratories, was carried out at the Imperial College of Science and Technology by G. F. Bloomfield, E. H. Farmer, and C. H. Miller (see Appendix).

With regard to the results obtained by these authors, it will be observed that the difference in chlorine content between the original chlorinated rubber and the expanded material is not great. The results may, as has been indicated, suggest that any difference in chlorine content between the original material and the ex-



Magnification about 37*
Figure 5—Sketch of
Piece from Middle of Ex-
panded Fiber. About Two
Fields Sketched.



Magnification about 37*
Figure 6—Sketch of
Piece of Outer Skin of
Expanded Fiber.
About two Fields
Sketched.

* The original sketches, which were at mag. 92, have been reduced for reproduction.

panded product is due to variation in the occluded solvent (carbon tetrachloride) and not to the elimination of either chlorine or hydrochloric acid during the expansion process. It will be observed in the case of comparable products Nos. 5 and 8 (both purified) that the chlorine content is practically identical. We are, therefore, forced to the conclusion that expansion is either purely a chemical or a physical process, *e. g.*, it may be brought about by occluded solvent, but this latter hypothesis is at least questionable. It fails to explain why, for example,* two specimens of the same commercial grade, which are practically identical as regards chlorine content, loss at 100°, and "free" carbon tetrachloride, should differ widely in their capacity for expansion. The two samples in question were obtained and examined at different times—after an interval of about 1 year—and it may be that, although apparently almost identical in composition, some slight modification in manufacture has influenced the stability. The specimens in question, however, as well as several other commercial grades of chlorinated rubber which do not yield good expanded products as such, expand readily on the addition of small quantities (from 5 to 20%) of liquids such as benzene or alcohol. In this connection it is interesting to note that expansion is promoted or activated by means of liquids which are either solvents or non-solvents so far as chlorinated rubber is concerned.

* See Nos. 21, 22, 29, and 30 (Bloomfield and colleagues).

On the other hand, we were able to satisfy ourselves that various substances such as water, sodium bicarbonate, and paraformaldehyde (*i. e.*, materials exercising considerable vapor or gas pressure at elevated temperatures) are without effect on expansion.

Direct experiments were made with a view of ascertaining whether any gas is evolved during the expansion process. For example, a sample during and after expansion was connected up with wash bottles containing potassium iodide, silver nitrate, and aniline and potassium hydroxide, respectively, but the results were negative. If there is any direct evolution of gas, it would seem that it is retained in the cells of the expanded product.

On heating either chlorinated rubber or the expanded product with aniline and caustic potash solution, phenylcarbamide was evolved in both cases, but neither chlorinated rubber nor the expanded product showed the carbylamine reaction when dissolved in toluene.

A conclusion that may well be drawn, therefore, is that chlorinated rubber, whether expanded or not, contains no free carbon tetrachloride. Possibly some carbon tetrachloride is loosely combined with the chlorinated rubber, the expansion process being caused by the release of this carbon tetrachloride. It is also possible that the carbon tetrachloride may be formed by decomposition of the chlorinated rubber as such.

Stability

On heating chlorinated rubber *A* (low viscosity) at 120° until the loss of weight was constant, losses of 6.0 and 5.4% were observed. Similarly chlorinated rubber *C* (high viscosity) lost 4.3% under these conditions. On the other hand, the expanded product made from grade *A* lost only 1.6%. On heating, both the original chlorinated rubber and the corresponding expanded product commenced to darken at about 175° and charred completely at 185°.

In another series of experiments on stability, the decomposition temperature was ascertained by heating in nitrogen and passing the issuing gases into silver nitrate. The decomposition temperatures of various specimens of chlorinated rubber and of the expanded product were as follows:

Sample	Decomp. Temp.
Chlorinated rubber <i>A</i> (low viscosity)	145°
Chlorinated rubber <i>A</i> (high viscosity)	150°
Expanded material <i>A</i> (low viscosity)	138°
Chlorinated rubber <i>B</i> (high viscosity)	108°
Chlorinated rubber <i>C</i> (high viscosity)	190°
Chlorinated rubber <i>D</i>	135°

The stability to light and to oven temperature at 100° was also tested on chlorinated rubber *A* and on the expanded product made from it. A solution of the two materials was painted on bright copper and the metal so treated was exposed under the conditions mentioned. Both were stable under these conditions.

Iodine Values

The iodine values of chlorinated rubbers *A*, *B*, and *C* (high and low viscosities in each case) and of the expanded product made from *A* were determined. Under the conditions of the experiment the iodine value of crepe rubber was found to be 234.3 but all the chlorinated rubbers and the expanded material examined gave results within 0.05 cc. of 0.1 *N* thiosulfate of the blank. That is to say, none of the chlorinated rubbers nor the expanded material showed any iodine value. This

strongly confirms the view that the change from chlorinated rubber to expanded chlorinated rubber is not of a chemical nature, although such evidence is, of course, not conclusive.

Modifications of Process

It has already been mentioned that while the production of the expanded product from certain commercial brands as such is difficult or impracticable, the addition of certain volatile liquids (either solvents or non-solvents for chlorinated rubbers) makes it possible to obtain an expanded product from them. Liquids such as benzene, toluene, xylene, or alcohol are added to the chlorinated rubber powder before expansion in proportions which may vary between say 5 to 20% to obtain good results. It has also been observed that an improvement may be obtained by the addition of plasticizers; for example, chlorinated rubber (*A*), which yields a very good result on expanding without any addition, gives still better results on addition of 6% of triacetin, or of tricresyl phosphate or of dibutyl phthalate mixed with 3% of toluene. The main improvement is that of giving increased strength to the product.

Practical Applications

While it is yet early to speak definitely regarding practical applications, it seems probable that the chief uses for the expanded product should be as an insulating material, for example, in refrigerators for perishable or changeable foodstuffs, and also where a light yet non-inflammable substance is required for the purpose of adding to or retaining buoyancy under various conditions (aircraft, speed boats, life-saving apparatus, and the like). Naturally, the extent to which such applications can be made depends largely on the cost of chlorinated rubber and of the expansion process. The latter, it is believed, on the large scale should be comparatively low. The cost of production of chlorinated rubber is still somewhat high, but with improved methods of production and increasing demand, it is probable that the ultimate cost will be of such an order that mass application will be perfectly feasible. On the Continent, certain grades are already marketed at about 10% above the selling price of nitrocellulose.

Acknowledgment

The authors are indebted to the Rubber Producers' Research Association, for whom this work was carried out, for permission to publish, and express their thanks to the members of the Modified Rubbers Research Committee for suggestions and advice. In connection with the molding experiments it is desired to thank Messrs. Ebonestos Insulators, Ltd., and Messrs. T. H. & J. Daniels, Ltd., for valuable assistance.

APPENDIX

The Composition of Some Chlorinated Rubbers

G. F. Bloomfield, E. H. Farmer, and C. H. Miller

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With a view to obtaining some information which might throw light on the nature of the expansion process and on certain differences observed in the readiness with which various chlorinated rubbers undergo expansion, the compositions of a number of chlorinated rubbers have been determined. For these determinations the commercial materials were dissolved in benzene and filtered free from insoluble matter, the solutions being then concentrated to small bulk under reduced pressure; the chlorinated rubbers were precipitated by the addition of methyl alcohol, washed and ground with chilled methyl alcohol, and finally maintained at 50–60° under high vacuum until constant weight was attained. The results of the various determinations are expressed in the table below.

No.	Manu-fac-ture	Description	Condition in Which Analyzed	C %	H %	Cl %	Total %	Qualitative Sulfur Test
1	A	High viscosity	Purified	32.1	3.33	64.2	99.6	Trace
2	A	Low viscosity	Purified	31.3	3.07	...*	97.2	Trace
3	A	Expanded from No. 2	Crude	61.6
4	A	Low viscosity	Crude	68.8
5	A	Same material as No. 4	Purified	65.4
6	A	Expanded from No. 4	Crude	67.6
7	A	Do., expanded after addition of alcohol	Crude	67.5
8	A	Same expansion product as No. 6	Purified	65.5
9	B	High viscosity	Purified	34.3	3.52	61.4	99.2	None
10	B	High viscosity	Crude	61.5
11	B	High viscosity expanded	Crude	60.5
12	B	Medium viscosity	Purified	30.3	2.83	67.1	100.2	None
13	C	High viscosity	Purified	31.3	3.23	64.9	99.4	None
14	C	Low viscosity	Purified	30.5	2.97	67.1	100.6	None
15	C	High viscosity	Crude	63.3
16	C	High viscosity expanded	Crude	63.1
17	D		Crude	60.8
18	D		Purified	34.4	3.53	61.5	99.4	None
19	E		Crude	67.0
20	E		Purified	30.2	3.68	65.7	99.6	...

* Figure unreliable owing to probable experimental error.

It will be observed that with one exception (*D*) the chlorine content falls 1–2% on purification. Now it is known that commercial brands of chlorinated rubber suffer a slow loss of weight on heating at 100° (Fol and Bijl, *Bull. Rubber Growers Assoc.*, April, 1932), and it has been further observed by us that under these conditions no hydrogen chloride is lost, but that some ammonium chloride is lost by sublimation (the ammonium chloride arising probably from chlorination of the nitrogenous non-rubber substances); traces of moisture are also lost. C. A. Redfern has observed that when a chlorinated rubber (*A*) is heated with aniline and caustic potash solution a pronounced carbylamine odor is produced, indicating that a part of the loss of weight is to be accounted for as loss of carbon tetrachloride occluded in the chlorinated rubber. Fol and Bijl have stated that *A* contains as much as 21% of absorbed carbon tetrachloride, but on close examination of their experimental results it is apparent that the argument on which this figure is based is fallacious, since no account is taken of volatile decomposition products other than

hydrogen chloride. We have here endeavored to obtain an estimate of the amount of free carbon tetrachloride present by a new method involving dissolving, precipitation, and subsequent determination of carbon tetrachloride in the mother liquors. The chlorinated rubbers (0.5 g.) were each dissolved in benzene (10 cc.) and precipitated by the addition of alcohol (20 cc.), the mother liquors were decanted, and the residue was redissolved in benzene and reprecipitated with alcohol: this process was repeated once more. The mother liquors were united and distilled, and it was observed that in no case did the distillate give any precipitate with silver nitrate; the chlorine content of each distillate was then determined by the method of Stepanov, and the results were calculated as carbon tetrachloride.

The following results were obtained:

No.	Specimen	% Carbon Tetrachloride
21	A Low viscosity new specimen	7.5
22	A Low viscosity obtained about 1 year previously	8.1
23	B High viscosity	5.3
24	B Medium viscosity	3.3
25	C High viscosity	3.4
26	D	1.7
27	E	8.4
28	Expanded material (from low-viscosity A)	6.3

It is apparent that D is the only chlorinated rubber which is substantially free from absorbed chlorinated solvent. The figures given must be regarded as approximate only, but serve as a comparative indication of the proportion of solvent present.

Redfarn has been unable to collect any evolved gases or vapors during the expansion process, and it indeed appears from the last of the above results that the major portion of the absorbed solvent remains in the porous expanded material.

The two specimens of A examined here are distinctly interesting, since some marked differences in the readiness with which they undergo expansion are reported elsewhere. These specimens were further examined as to chlorine content and loss of weight on heating (*i. e.*, moisture, solvent, and ammonium chloride); it should be noted that these were different specimens of A from those analyzed previously.

No.	Specimen	Loss of Weight during 6 Hr. at 100°/0.1 Mm.	Chlorine Content
29	A (new)	0.75%	68.8% crude 65.9% ptd.
30	A (old)	0.6%	68.9% crude 65.8% ptd.

The very small loss of weight is indicative of the extraordinary tenacity with which the solvent is held.

That expansion may indeed be caused by the presence of solvent was further tested by dissolving a mass of expanded material in benzene, precipitating with alcohol, and subjecting the precipitated material to expansion. It was found by Schidrowitz and Redfarn to expand readily, provided that it contained a little solvent or alcohol, indicating that the original expansion had not involved any change in structure or chemical nature of the material such as would interfere with further expansion.

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Rubbone

H. P. Stevens and W. H. Stevens

Of all the reactions which natural rubber undergoes, oxidation next to vulcanization, may be said to rank in the first place. For not only does the life and usefulness of all raw and vulcanized rubber depend on the course of this reaction, but attempts to create useful oxides may be regarded as based on the same reaction. It has already been shown that, by the catalytic oxidation of rubber, solutions of greatly reduced viscosity and/or increased concentration are obtainable.¹ Thus, a 50 per cent solution of rubber which will flow at normal temperatures can be made by incorporating 2.5 per cent of cobalt linoleate on the mill, subsequently "letting down" in white spirit or other solvent by means of an internal type of mixer. The mechanism of the oxidation of rubber is a complex and still incompletely solved problem, but a reasonably acceptable explanation of this reduction in viscosity is that it is due to a disaggregation of the rubber micelle, whereby a very small amount of chemically combined oxygen is enabled to effect a very large physical change in the character of the colloid. This change is promoted by catalysts, such as the ordinary paint driers, and there appears to exist an analogy between the drying of paint and the disaggregation of rubber solutions, but it is interesting to note that whereas copper soaps have substantially no effect on the drying of linseed oil, they do reduce the viscosity of rubber solutions appreciably.

Solutions of rubber containing catalysts have been "blown" by bubbling air, oxygen or ozonized air through them while maintained at raised temperatures by suitable means. The experiments covered a great variety of conditions, including different solvents, different types and concentrations of rubber and catalyst, mixed catalysts and a variety of temperatures and blowing conditions. It was found that under suitable conditions the oxidation of the rubber could be taken to a stage where the cobalt linoleate itself became oxidized and was precipitated from the solution. After filtering, the resulting solutions were evaporated to yield an oxidized rubber resin.

A standard procedure has been developed for the production of this rubber resin,² or "Rubbone" as it is conveniently termed,³ as follows. A solution of milled blanket crepe in white spirit is made by dissolving 20 parts by weight of rubber in 80 parts by weight of solvent, adding 0.5 part of cobalt linoleate, and aerating at 80° C. until a sample drawn off from the bulk shows a quick separation of sediment and a clear supernatant solution of the resin. The solution is clarified by "tanking" or centrifuging and is then distilled by steam or in vacuo to separate the resin.

Properties and Applications

The properties of Rubbone are of considerable interest. From a practical point of view the oxidation reaction has not previously been of much interest except in so far as it has been possible to prevent it or retard it. No use has been found for an oxidized rubber as such, though the oxidation reaction has been utilized as a preliminary to chlorination,⁴ and the ordinary mastication process is now generally recognized to entail a very slight degree of oxidation.

The properties of Rubbone indicate that an oxidized rubber may find application as a component of paints, varnishes, and enamels, for electrical insulation, particularly in the impregnation of coils and the like, and possibly for molding purposes.

Broadly speaking the material is capable of further oxidation (drying) and of thermosetting. In the latter case the pure Rubbone yields a soft elastic substance similar in character to a polymerized tung oil gel.

The composition of Rubbone approximates $(C_6H_5)_2O$. It is a clear, sticky amber semi-solid of the consistency of thick treacle; that is, it will just flow at normal temperatures. A sample prepared in the standard method from acetone-extracted crepe had the following characteristics:

Formula	$(C_6H_5O_{0.45})n$
Acid value	5
Saponification value	60
Iodine value	305
Specific gravity	0.966 (at 27° C.)
Refractive index	1.519 (at 28° C.)

On exposure to air, Rubbone hardens slightly on the surface, which becomes non-tacky and solid. This change is accompanied by a small increase in weight, indicating further oxygen absorption. On heating, the resin becomes more fluid, and is quite fluid at 100° C. When maintained at temperatures above 100° C. a thermosetting takes place through the mass, at the same time as oxidation proceeds on the surface exposed to the air. Heating for 24 hours at 140° C. is necessary to fully set the resin so that it becomes insoluble in white spirit, etc. At 200° C. it sets in 1.5 hours, though liable to porosity, whereas at 100° C. it requires 50 hours.

It has been found possible to accelerate the setting of the resin by the addition of certain reagents. These "accelerators" have been discovered empirically, and at present it is difficult to understand how they function. Thus, with 5 per cent of potassium permanganate the heating time at 140° C. is reduced from 24 to 7 hours, but potassium bichromate, manganese dioxide, and certain other oxidizing agents have no effect. On the other hand certain antioxidants promote hardening. The following table details the behavior of some of the substances tried:

Reagent	Per Cent on Resin	Temperature ° C.	Reaction
Potassium permanganate	5	140	Hardens
Potassium bichromate	5	140	No hardening
Manganese dioxide	5	140	No hardening
Red lead	5	140	No hardening
Cobalt linoleate	5	140	No hardening
Diphenylguanidine	5	140	No hardening
Zinc diethyldithiocarbamate	5	140	No hardening
Mercaptobenzothiazole	5	140	No hardening
Ethyldiene-aniline	5	140	Softening agent prevents oxidation
Pyridine	10	105	Softening agent
Tetramethylthiuram disulfide	5	140	Hardens
Zinc isopropylxanthate	5	140	Hardens
Benzoyl peroxide	5	140	Hardens
Sodium peroxide	5	140	Hardens
Ammonia	..	Room temperature	Hardens
Ammonium chloride	10	150	No hardening
Hexamethylenetetramine	10	100	Hardens slowly
Urea	10	100	Hardens slowly
Thiourea	10	100	Hardens
"Nonox S"	5	120	Hardens slowly
"Nonox H"	5	120	Hardens

The disadvantage of most of the "accelerators" is that they cause porosity, which is not inherent to the resin itself. The best results are obtained with ammonia, urea, thiourea, and "Nonox S."

The unsaturation of Rubbone can be reduced by sulfur addition, as well as by polymerization or addition of further oxygen. This probably accounts for the presence of tetramethylthiuram disulfide as an "accelerator" in the above list; the effect has really been that of a vulcanization. The reverse process of preparing Rubbone from a lightly vulcanized rubber is also possible. In one experiment a soft vulcanized rubber was dissolved after acetone-extracting the vulcanizate, followed by refluxing in white spirit (10 hours at 130° C.). After oxidation this yielded a resin slightly tough and elastic but generally similar to Rubbone. It contained 1.3 per cent of combined sulfur. Products prepared by direct vulcanization either to the soft or to hard rubber stage do not have attractive properties, and are harder and less tacky, but frequently brittle or friable. Further work, however, is required before all the possibilities are exhausted. A tough elastic skin can be formed on Rubbone by dipping in sulfur chloride solution, or by treatment with halogens which are convenient methods where a surface effect is suitable. Owing to its fluidity at raised temperatures, Rubbone is especially valuable for impregnating electric wire coils, since no solvent or other impregnating medium is required. On baking the impregnated coil the solid mass of the Rubbone thermosets to an elastic insulator, and the surface "case-hardens" by oxidation. In this condition the Rubbone is substantially water- and oil-resistant. Distilled water absorption at room temperature of a film of hardened resin (24 hours at 140° C.) gave the following results:

In 24 hours	0.25 per cent
In 48 hours	0.45 per cent
In 168 hours	0.75 per cent

No whitening or discoloration of the film occurred.

The above figures, obtained with the standard resin, are reduced still further by special modifications in composition or method of preparation.

Further work on the preparation and utilization of Rubbone is in progress.

References

- Trans. Inst. Rubber Industry*, 9, 247 (1933); RUBBER CHEM. AND TECH., 7, 486 (1934).
- British Patent 417,912.
- We are indebted to Professor G. T. Morgan for this suggestion as to nomenclature.
- British Patents 413,559, 415,438.

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March, 1935.]

Rubber in Paints

H. P. Stevens, W. H. Stevens, and Noel Heaton

As a result of our previous publication (**RUBBER CHEMISTRY AND TECHNOLOGY**, 7¹ 486 (1934)) it is now well known that oil gloss and flat paints which contain a small proportion of rubber have greatly improved flowing and non-settling properties. A flat paint made with a medium containing equal parts of rubber and stand oil requires no stippling to produce a smooth surface, but will flow out perfectly when brushed on, while pigments which quickly settle out to a hard cake in a plain oil medium can be used in the oil/rubber medium with much greater safety. Such paints soon become dust-dry after brushing out, and also have the advantage of "keeping open," thereby enabling the decorator to brush out a large surface without fear of the paint drying at the edges and so preventing a clean "join up." Adhesion is also good, and the paints can be used equally as well for undercoatings as they can for flat finishes.

In ready-mixed oil paints the addition of a smaller proportion of rubber is sufficient to give the paint the required flowing properties, 15-20 per cent of rubber on the oil being a suitable proportion.

Matters of first importance are the method of adding the rubber and the stage at which it is incorporated into the paint. The obvious way to add the rubber is in the form of a solution in the usual paint solvents. Raw rubber, however, gives extremely viscous solutions, and additions of only small proportions necessitate excessive thinning. Raw rubber also has a great tendency to cause the paint to thicken ("liver up").

These difficulties have been overcome by milling the rubber, and adding a proportion of a paint drier (soluble in the solvent). A solution of rubber much reduced in viscosity can thus be produced, which when added to a paint does not cause "livering up."

An addition of 2.5 per cent cobalt linoleate to the rubber appears to be sufficient to give the maximum reduction in viscosity. A 50 per cent solution of this modified rubber in white spirit should be used, and a satisfactory method of preparing the solution has been found by using a horizontal pug mill or internal mixer. The solution should not be kept at a lower concentration than 50 per cent as there is a tendency for thinner solutions to reduce still further in viscosity and to lose some of their properties.

In preparing a paint it is advisable to mix the oil, rubber solution and the necessary thinners to a homogeneous solution and then grind in the pigments, etc. Any of the usual pigments and fillers can be incorporated.

As examples of formulas for rubber containing paints the following are suggested.
(Note. The 50 per cent modified rubber solution is called Solution B.)

FLAT PAINTS

Formula No. 1

Lithopone	65
Titanium white	65
Terra alba	12.5
Magnesium carbonate	2.5
Stand oil	10
Solution B	20

Terebene	1	=	Lead .033
White spirit	35		Cobalt .004

Formula No. 2

Lithopone	150
Stand oil/wood oil (3/1)	10
Solution B	20
Terebene	1
White spirit	30

(An egg shell finish can be obtained by reducing the proportion of pigment.)

READY MIXED GLOSS PAINTS**Formula No. 3**

Zinc oxide	100
Pale boiled oil	62.5
Solution "B"	25
Terebene	2
White spirit	10

Formula No. 4

Zinc oxide	50
Titanium white	50
Pale boiled oil	62.5
Solution "B"	25
Terebene	2
White spirit	10

Formula No. 5

Lithopone	80
Zinc oxide	20
Pale boiled oil	30
Solution "B"	15
Terebene	1
White spirit	20

Formula No. 6

White lead	100
Pale boiled oil	30
Solution "B"	12
Terebene	1
White spirit	6

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Rubber in Lubricants

H. P. Stevens, W. H. Stevens, and M. B. Donald

As long ago as 1853 it was found that rubber was a suitable addition to oils to improve their lubricating properties. Thus rosin oil¹ was rendered suitable for lubricating machinery, locomotives, wagons, etc., by adding as much of a 1-2 per cent stock solution of rubber in rosin oil to further amounts of oil as deemed suitable. The rubber was cut in thin strips, masticated, and allowed to dissolve in the rosin oil in a hot water bath. A lower temperature could be used by prolonging the time of immersion. A subsequent patent² and formulas in a book by Brunner,³ propose dissolving the rubber in turpentine and adding it to fish and vegetable oils in proportions of about 5-10 per cent. As will be shown later, these proportions are probably too large to be satisfactory, and moreover at that period the recipes were not economical.

In 1855 a patent⁴ was taken out by Hyde, which in view of our own observations must be regarded as a very remarkable piece of work. After stating that mineral oils for lubricating machinery at temperatures of 600° F. or over require admixture with castor, sperm, or rape oil, he draws attention to the fact that, on keeping at 212° F., or for several days in sunlight, the mineral oils develop a sludge. The addition of rubber to mineral oils, he states, "exerts a most remarkable action in giving permanence to them . . . and at the same time improves the lubricating or truly oily character of the oil, and the changes under the influence of high heats or the sun's rays are in like manner retarded or prevented for a longer time so as to give a degree of permanency and lubrication such as no other known oil or mixture possesses when tested by lubrication indicators. When more than 2 per cent rubber is added the valuable qualities are in every case impaired, and even less than 1 per cent is usually all that need be combined; 0.5 per cent will give durability and lubrication much beyond that of sperm oil." He introduced the rubber by suspending it in a cloth bag in the mineral oil at 80-150° F.

Subsequent patents⁵ do not suggest very great improvements. Brinch in 1889⁶ patented a mixture with as low a rubber content as 0.1 per cent. He states that one or two days are necessary for solution to take place in the cold. More recently Rigby⁷ has proposed the use of latex in paraffin (kerosene), but this is unsuitable from the point of view of excessive volatility, while Asprey⁸ has recently suggested the use of latex in mineral oils.

Before these facts had been ascertained, a trial was made of some rubber mineral oil lubricant, prepared by dissolving 2 per cent milled rubber in spindle oil with the aid of heat, on the conical headstock bearing of a small lathe, which had been giving continuous trouble in seizing up owing to a slight scoring of the bearing surfaces. The rubber lubricant was added 3.5 years ago, and the bearing has given no trouble since. Other experiments confirmed the value of rubber containing lubricants for cold bearings, *e. g.*, line shafting, etc. In view of this success it was decided to carry out further research on the subject.

The first point to consider was the question of viscosity, and a mineral oil with 50.7 sec. flow on a Redwood No. 1 instrument and 0.870 specific gravity at 60° F. was chosen. The results are shown in Fig. 1, and it will be seen that the increase in viscosity is maintained over the temperature range 60-200° F. for any given addition of rubber. The viscosity is increased five-fold for a 2 per cent addition and twenty-five fold for a 5 per cent addition. It will be seen that the addition of

rubber provides a means of increasing the viscosity of an oil without, however, increasing it unduly at low temperatures when the bearings are cold and the machinery or engine is being started up. (A number of mineral oils contain crystalliz-

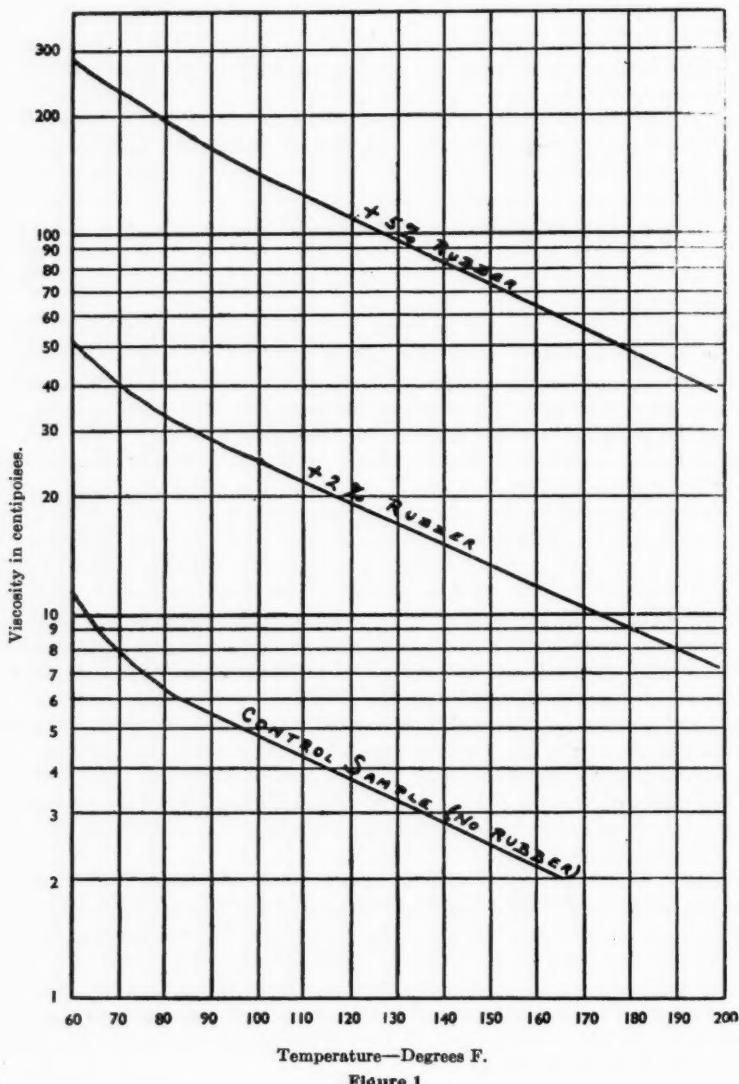


Figure 1

able bodies similar to paraffin wax, which cause a very undesirable increase in viscosity in cold bearings.) The rubber also helps the lubricant to remain in the bearing, and avoids drips, which is obviously valuable for overhead shafts. It has been stated that Asprey's latex⁹ lubricant was satisfactorily used on a printing press

running continuously for a month, and the consumption was 7 gallons against a previous consumption of 24 gallons of normal high grade oil. It has also been stated that a 1928 Essex motor car was prone to engine overheating, but after using the above lubricant the engine temperature dropped to normal and the car gave improved results.

The second point to consider was the effect of rubber on the "oiliness" of the lubricant, *i. e.*, the improvement in lubrication obtained by using rubber when working at very slow speeds as in starting or in reciprocating motion. The static coefficient of friction was determined on a Deeley oil testing apparatus with the following results:

Bayonne (New Jersey) oil	0.124
Bayonne (New Jersey) oil + 2 per cent rubber	0.103
Medicinal paraffin	0.092
Medicinal paraffin + 1 per cent rubber	0.084
Diesel oil + 1 per cent rubber	0.135
Diesel oil + 2 per cent rubber	0.127
Diesel oil + 5 per cent rubber	0.125

It will be seen that the addition of rubber up to 2 per cent has a beneficial effect on the "oiliness" of the lubricant, and these results confirm those of Hyde in 1855.

The third point is related to the influence of rubber on the oxidation of the lubricant. The oxidation test of the Institution of Petroleum Technologists consists of blowing air through the oil at a temperature of 150° C. in the presence of copper foil as a catalyst. Bayonne oil with and without the addition of 1 per cent rubber was blown with air for 16.5 hours. The results were as follows:

Plain oil sediment	0.0044 per cent
Oil + 1 per cent rubber sediment	0.0038 per cent

We thus see that once again the results obtained by Hyde have been confirmed; *i. e.*, that oil is more resistant to heat when it contains rubber.

While no attempt has been made to ascertain the optimum quantities of rubber required for the various lubricants, the results of this preliminary investigation show definitely that its use is attended by a number of improved qualities of the oil. Additions, such as fatty acids, have been proposed from time to time to improve the "oiliness" or other properties of lubricants, but rubber is substantially non-acid and therefore non-corrosive, and appears to improve not only one property but a number of them.

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[Translated by Norman Bekkedahl for Rubber Chemistry and Technology from the *Chemisch Weekblad*, Vol. 31, pages 614-615, 1934.]

Preparation from Rubber of Plastic Materials Suitable for the Manufacture of Films and Threads

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The investigation describes a method for the preparation from rubber of plastic materials having properties described in the title. The products were made by acting upon rubber with gaseous hydrochloric acid.

It is shown that hydrochloric acid under certain conditions can be added to rubber, with formation of products suitable for the manufacture of films and of threads which may be used in the textile industry. These conditions can be so chosen that they are of technical application.

The preparation and application, though not always for the purpose given here, of chlorinated rubber has long been known.¹ The use of this product in several industries, *e. g.*, the dye industry, is objectionable because of the high chlorine content, which is about $\frac{2}{3}$ of the weight.² The addition of HCl to rubber has likewise long been known as is shown by the investigations of Weber³ and of Harries.⁴ There is also evidence in the patent literature⁵ that work has been done along the same lines as that studied in the present investigation, and this earlier work was probably suggested by the methods of Weber and Harries. Both investigators prepared the addition product of HCl and rubber by passing hydrogen chloride gas into a solution of rubber in chloroform after cooling to a temperature below 10° C. (Weber). The addition product, which in the following text will be called HCl-rubber, was separated from the mixture by the addition of alcohol, in which the HCl-rubber is insoluble, so that precipitation ensued. The methods of Weber and of Harries were such that they were not of technical application. The principal objection to their work is the use of very dilute solutions. Harries started with a solution of rubber of very low concentration in benzene which he added to chloroform. He thus obtained a solution, the concentration of which was not greater than 3 per cent (1 kg. of rubber in not less than 20 liters of chloroform). He referred to it as a suspension and not as a solution.

From the results of these methods we have come to the conclusion that it is impossible to prepare in this manner strongly concentrated rubber solutions. We have, however, obtained in the HCl-rubber a product which has several technical applications, such as the manufacture of films.⁶

For reasons of economy, we have gone over to the use of more concentrated solutions, which can be obtained by subjecting the rubber to a plasticizing process.⁷

Preparation of the Product

Carbon tetrachloride and benzene were both considered as solvents for the rubber. Under the conditions used, the CCl_4 did not give satisfactory results. In a test in which CCl_4 was used as solvent, a 0.5-1.0 per cent solution was obtained from unplasticized rubber. Experiments were carried out at high temperatures (72-77° C.) as well as at low temperatures (0-1° C.). In all cases, however, the quantity of rubber transformed was very small. The low temperature gave a much

better yield than the high temperature, as was to be expected. In the first case the reaction product contained 13.7 per cent of chlorine, in the second 1.4 per cent. The addition of AlCl_3 as catalyst at 0–1° C. gave unsatisfactory results.

However, when benzene was used as a solvent with a 2 per cent unplasticized rubber solution, complete transformation into HCl-rubber (having the empirical formula $\text{C}_5\text{H}_9\text{Cl}$) was obtained at a temperature of 16.5–19° C. Similar results were also had with more concentrated solutions, which were obtained by solution of plasticized rubber. The use of plasticized rubber makes it possible to work with 10 per cent or stronger rubber solutions.

The technic of the process was always the same. That part of the rubber which had not dissolved or been plasticized by the heating process was subjected to treatment with hydrogen chloride gas (dried by sulfuric acid) by leading it into the solution to saturation. Here it was allowed to stand for 16 hours for further action to take place. The final product was obtained, as is described in the literature, by adding the mixture to alcohol, shaking, filtering, washing, and finally drying *in vacuo* at low temperatures.

Properties and Uses of HCl-Rubber

The HCl-rubber prepared in this manner is capable of being made into films and being spun into threads. The films are prepared by spreading out very viscous solutions of HCl-rubber in chloroform which have been filtered under pressure. The pressing out is done on a plate of glass at ordinary temperatures. The solvent is first allowed to evaporate in air at room temperature and later at 45–50° C. The outer surface of the film is glazed, bright and transparent, whereas the back of the material feels soft. Several tests of the tensile strength and elasticity gave favorable results. Softening agents can be added to these films during their manufacture. In general they weaken the films and increase their elongation. In certain cases the softening agents changed the surfaces of the films. Whereas the addition of tricesyl phosphate (10 per cent of the quantity of HCl-rubber causes no change, triacetin, wood oil, and linseed oil have a favorable influence on the properties of the film. It is also possible to color the films by addition of soluble colors to the solution from which the films are made. The films have good adhesion to different metal surfaces, such as copper, zinc, and lead. The properties of these films can be improved further by the addition of other plastic materials, such as Albertol resin.

The threads are manufactured by the dry spinning process. Pressure is used to filter the 7 per cent solution of HCl-rubber in chloroform. The surface of the thread is a matt white. Preliminary experiments indicate that the wet spinning process is possible from solvents such as alcohol, acetone, etc.

The question of durability is of the greatest importance in the application of the product to the film and textile industries.

Durability tests were made on the reaction product obtained from a 30-minute plasticized rubber:

(a) The combustibility is small; in the flame the material burns well, yet outside it has considerable resistance.

(b) A study of the resistance of the films towards various chemicals was made by the use of weighed strips of film, which were dried for 2.5 hours at 50–52° C., put into the solution under test, and left there for 6 days at room temperature (about 20° C.). After rinsing in water and drying all samples in the same manner, the loss of weight was determined and the surface of the film examined.

Hydrochloric acid (d. 1.19), 2 N hydrochloric acid, 20 per cent potassium hydroxide, 2 N potassium hydroxide, soap solution, distilled water, and 4 N sulfuric

acid gave a loss of weight of 0.5–1.2 per cent, while the surface of the film was not changed. With concentrated sulfuric acid, the loss in weight was 3.4 per cent, and the surface turned brown. Concentrated nitric acid crumbled the film. The product was, as was to be expected, not completely thermostable, and continued heating at 55–60° C. gave a noticeable loss of HCl.

On the basis of the above-mentioned statements, we must conclude that HCl-rubber offers technical possibilities.

It is hoped to extend the investigation further in different directions.

Summary

A technical process is described for the preparation of HCl-rubber. Plasticized rubber was used to obtain highly concentrated rubber solutions in C₆H₆.

The HCl-rubber was proved to have properties useful in technical applications as film material.

By the method of dry spinning, threads were also obtained. In so far as they were examined, the films and threads were of good quality.

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- ⁵ See U. S. patent 1,627,725; 1,841,295; 1,852,294; 1,773,101. Netherland patent 64,415.
- ⁶ Thies and Clifford, *Ind. Eng. Chem.*, **26**, 134 (1934).
- ⁷ We thank the Rikjerubberdienst te Delft for the sample of plasticized rubber.

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Properties of Latex-Insulated Wire

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In 1863 latex was proposed and actually used to insulate wire. Siemens had the happy thought of employing this material to cover conductors and actually went so far as to obtain patent protection for his idea. From that time until recently, there has been practically nothing accomplished in the manner directed by Siemens. In fact, no commercial insulation material resulted from the idea proposed in the middle of the nineteenth century.

It is not hard to see why such a plausible idea was abandoned. The insulation obtained in the manner disclosed by Siemens was not nearly as good as the other known methods for insulating wire. Conductors covered by the method then proposed could not be used in water or where any moisture was present. There were too many water-soluble materials in the latex; and as no method was known at that time to remove these materials from latex without coagulating the latex itself, no further development was accomplished.

Latex Purification

Only around 1920 methods began to be developed for purifying latex. It was realized that, if latex could be purified and free from its nonrubber constituents, there would be many commercial uses for it. The technicians in this field set to work, and, in rapid succession, filtering, dialysis, centrifuging, and creaming of latex became not only laboratory procedures but practical methods. The problem now resolved itself into finding which one of these purification methods appeared most useful, and to what extent such a method would have to be followed in order to obtain the highest amount of electrical insulation. At present these questions are not completely answered. We do not yet know what the limits will be for this type of insulation. In other words, as in other fields there is always room for improvement. Not until a stable, purified, practically 100 per cent rubber latex was obtained did the field of electrical insulation by the use of latex seem at all practical.

The facts are easily visualized from an examination of the physical and chemical properties of multicreamed latices purified in any one of the ways mentioned:

Latex	Surface	Acetone	Nitrogen	Ash	Water Absorption after 100 Hr. at Room Temp.
	Tension Dynes/cm.	Extract %	%	%	Mg./sq. cm.
Normal	34.7	5.20	0.70	1.0	13.5
Once-creamed	35.2	3.54	0.33	0.42	8.9
Twice-creamed	38.5	2.83	0.24	0.15	3.6
Thrice-creamed	39.1	2.48	0.10	0.09	1.8

The proportions of nonrubber constituents are remarkably decreased by this creaming process, and at the same time the water absorption is greatly diminished.

Water Absorption

A review of the literature of rubber compounds used for insulation shows definitely that materials introduced into rubber not only must be nonconductors themselves but also must not take up water. The importance of water absorption in an insulating compound is stressed by all investigators attempting to improve insulation. For this reason the simplest and most conclusive test as to whether a particular type of rubber, or any other material, will be useful for insulation purposes, is to measure its water absorption. A few tests for various types of rubber are included in Table I.

TABLE I. WATER ABSORPTION AT ROOM TEMPERATURE OF FILMS FROM MULTICREAMED LATTICES

Type of Latex Film	Water Absorption in Distilled Water after:			
	25 hr.	50 hr.	75 hr.	100 hr.
Milligrams per square centimeter				
Normal	12.1	13.0	13.3	13.5
Once-creamed	4.8	6.2	7.6	8.9
Twice-creamed	1.4	2.2	3.0	3.6
Thrice-creamed	0.9	1.4	1.6	1.8

The films on which the absorption tests were made were prepared as follows:

The latices were treated as indicated and then were spread on a smooth surface and allowed to dry at room temperature, producing a film with a thickness of around 0.015 inch (0.038 mm.). They were then dried further in a vacuum desiccator containing sulfuric acid. In the case of latices containing no vulcanizing ingredients, it was easy to determine from the clarity of such films when the films were completely dry. Weighed samples were then soaked in water and removed from time to time, the surface water was blotted with blotting paper, and the sample was reweighed to determine the increase in weight. The results are reported in milligrams of water absorbed per square centimeter of surface exposed.

Table I shows that, as latex is purified, the water absorption greatly decreases until, after sufficient operations, it is practically zero.

Up to the time that these developments in the purification of latex indicated the great possibility of using latex for insulation, ordinary crude rubbers such as pale crepe and smoked sheet were used for this purpose. The following table gives a

comparison of the water absorption of such rubbers with that of a fair sample of a purified latex at room temperature:

Rubber	Water Absorption in Distilled Water after:			
	25 hr.	50 hr.	75 hr.	100 hr.
	<i>Milligrams per square centimeter</i>			
Pale crepe	1.4	1.9	2.2	2.5
Pale crepe*	2.0	2.9	3.3	3.9
Smoked sheet	3.9	5.1	5.9	6.6
Triple-creamed latex	0.9	1.4	1.6	1.8
Triple-creamed, acid-coagulated	0.5	0.6	0.6	0.6

* Boggs and Blake, IND. ENG. CHEM., 18, 224 (1926).

The results on two samples of pale crepe from entirely separate sources by different investigators show variation, and also the sample of triple-creamed latex shows considerably less water absorption than either pale crepe or smoked sheet.

Advantages of Latex Insulation

In the days of Siemens, latex-insulated wire was thrown out on account of poor quality. Now since the quality requirements have been met, there are many advantages in the use and manufacture of latex wire as distinguished from the usual methods.

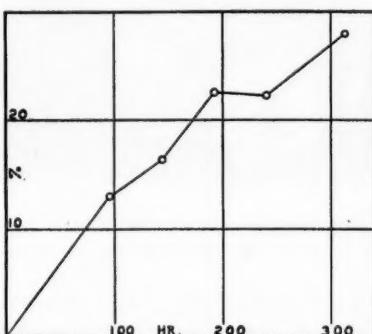


FIGURE 1. DECREASE IN TENSILE STRENGTH WITH OXYGEN BOMB AGING (COMPOUND 784)

compound and subsequently passed vertically into further drying chambers. This process is continued until the desired thickness of rubber is obtained on the conductor. The latex compound may be either vulcanized or unvulcanized. The type and temperature of the drying chambers and the resultant physical and electrical properties of the conductor will to a great extent be influenced by whether or not the latex has been prevulcanized or vulcanized during a drying cycle. The process is very simple, easy to control, and inexpensive to operate. The fact that the conductor leaves the latex in a vertical direction insures a coat of latex uniform all around the conductor. In other words, in the parlance of the insulation engineers, the

In the simplest manufacturing process for preparing latex wire, the conductor is led into a container holding a properly purified and compounded latex and is then passed upwards in a vertical direction into a drying chamber where the latex is heat-coagulated. Then it is brought down into another bath of latex com-

conductor at the conclusion of the operation is properly centered. There are no thin spots in the insulation. This property is a distinct advantage and manifests itself in the following ways:

- (1) Thinner wall of insulation to obtain the same equivalent electrical result.
- (2) Lesser amount of compound used to obtain the same equivalent electrical result.
- (3) A considerable reduction in weight for the same length of insulated conductor.
- (4) Reduced cost in any braiding or covering of this insulated conductor.

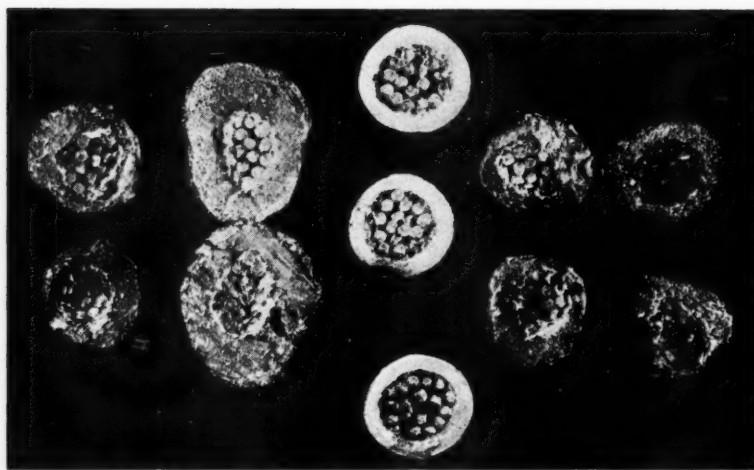


FIGURE 2. CROSS SECTIONS OF INSULATED WIRES
A. Latex treatment B. Extrusion method

All of these improved qualities have been obtained with no sacrifice of electrical insulation, strength, or age resistance of the rubber compound.

Early in the manufacture of latex wire, the U. S. Government realized the advantages of this material, especially in the work of the Army Signal Corps, Marine Corps, and Forest Service where a large amount of wire is used for communication purposes. The same length of insulated wire with equally good electrical resistance could be obtained at a decrease of 50 per cent in the weight.

Electrical Properties

In order to give some idea as to the insulating characteristics of latex wire, data on electrical characteristics are included. The following table gives the difference in the leakage of two films of rubber of comparatively the same thickness when subjected to a potential of 10,000 volts after soak-

ing in water for various time intervals. One of these films was prepared from a triple-creamed latex, the other from once-creamed latex. Here again is shown the value of triple-creaming for the removal of non-rubber constituents:

Time in Water Hours	Leakage at 10 Kv. for 1 Sq. In. (6.5 Sq. Cm.) Area	
	Once-creamed, 0.048-in. (1.22-mm.) latex	Triple-creamed, 0.04-in. (1.04-mm.) latex
0	0.057	0.059
48	Broke at 8 kv.	0.065
78	...	0.067
101	...	0.065

Although the once-creamed latex was of no value after 48 hours, the triple-creamed latex was still in excellent condition after soaking in water for 100 hours.

The insulation resistance of latex wire if properly prepared is remarkable. This is well illustrated in the following data on a triple-creamed latex after being soaked in distilled water:

Breakdown Voltage, Dry	Insulation Resistance after:				
	0 hr.	16 hr.	24 hr.	40 hr.	156 hr.
<i>Megohms per 1000 feet (305 meters)</i>					
828	8980	24,420	44,700	44,700	48,000

These values were obtained on a wire with an insulation thickness of approximately 0.016 inch (0.406 mm.). The resistance per 1000 feet actually increased over the first 24 hours, practically coming to a constant value at that time and continuing constant through 150 hours. The breakdown voltage is very high—in fact, about the upper limit for rubber. The high insulating quality of latex wire is as follows:

Time in Oxygen Bomb Hours	Insulation Resistance on Typical Factory Sample after Soaking in Water for:		
	22 hr.	94 hr.	190 hr.
	Megohms per 1000 feet (305 meters)		
4800	21,000	20,200	18,800
	Aging Tests		
	Tensile Strength	Stretch	
	Lb./sq. in. (kg./sq. cm.)	%	
Green	3781 (265.8)	850	
24	3965 (278.7)	850	
48	3689 (259.3)	840	
96	2969 (208.7)	840	

These data represent tests made on an insulated run-of-the-mill latex wire obtained from daily production. No attempt was made to pick a wire of particularly high insulation resistance. Here again the insulation resistance rises until a constant high value is reached—in this case, around 20,000 megohms per 1000 feet. Also, during the period of aging only a small decrease in tensile strength occurred.

In order to give a clear picture of the usual results obtained on aging latex-insulated wire, Figure 1 gives results with compound 784 to show its extremely good aging qualities.

At present a direct comparison of latex-insulated wire and wire obtained by the extrusion process is not possible. This is primarily due to the fact that it is difficult to make a centered wire by the extrusion process with the same wall thickness as that obtained by the latex process. At the present time any such direct comparisons would be vitiated by the unevenness obtained by the extrusion process. However, it is reasonable to suppose that, if such a comparison were possible and were carried out, electrical tests would be certainly as good and probably superior in the case of the latex process than in the case of the extruded material.

In order to give a clear picture of the really vital improvement in insulating conductors by the use of latex, Figure 2 gives cross sections of wire insulated by the latex method and by the ordinary extrusion method. The samples of extruded wire were obtained at random from different manufacturers. The latex samples were obtained from factory runs in this factory; no special precautions were taken. The picture represents the actual type of results which can be expected from the two processes.

All of the above information indicates that perfect centering combined with outstanding electrical properties has thus been made possible by the modern development of latex insulating methods.

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Koroseal, A New Plastic Some Properties and Uses

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Rubber has found its widest use in industry because its properties can be altered and improved by compounding and cure to give strong, flexible, resilient products which are resistant to abrasion, impervious to fluids, electrically insulating, and relatively inert chemically. For such other desirable characteristics as resistance to oils and solvents, and freedom from attack by air, sunlight, and oxidizing materials, skillful compounding has brought marked improvements, but even better properties are needed to meet the demands of modern industry.

The search for synthetic rubbers has been stimulated not merely by the desire for an economically independent source of supply, but also with the hope that there might be obtained materials having properties superior to the natural product. Whitby and Katz (4) have published a comprehensive historical treatise dealing with the development of numerous synthetic rubbers which have appeared in the last few years.

It has been believed that linear polymers obtained from dienes hold most promise for the preparation of rubber-like materials. Carothers (1) has studied the relation between the structure of dienes and the types of polymerization products which may be obtained therefrom. On the basis of these data he inferred that, from the standpoint of their polymerization products, the best dienes will be of the type $\text{CH}_2:\text{CXCH}:\text{CH}_2$, in which X is an activating group other than alkyl or aryl. In general it has been found that there may be obtained polymerization products with physical properties equal to, or often superior to those of natural rubber, and with marked resistance to the action of solvents and chemicals. Among the many types of organic materials which will polymerize, the vinyl compounds only recently have been modified suitably to yield commercial rubber-like materials.

In 1927 Ostromislensky (2) claimed that the polymerization products of vinyl chlorides might be divided into several classes according to their solubilities. The first, or acetone-soluble portion, he chose to call α -caouprene chloride. Likewise, the second, or chlorobenzene-soluble portion, he named β -caouprene chloride. The substantially insoluble portion, he termed γ -caouprene chloride. This latter tough, horny, heat-stable material has been shown to be substantially un-

affected by sunlight or by hot or concentrated oxidizing agents.

Semon (3) has shown that, although the completely polymerized vinyl halides are insoluble in practically everything at room temperature, they are soluble in a large number of materials at a sufficiently high temperature. He disclosed the formation of rubber-like gel structures by the treatment of highly polymerized vinyl halides with plasticizers at an elevated temperature followed by cooling. These products were given the name "Koroseal" and have served as a basis for the developments of this new class of materials.

The generic term "Koroseal," however, refers to a broad class of compositions with properties varying from those of

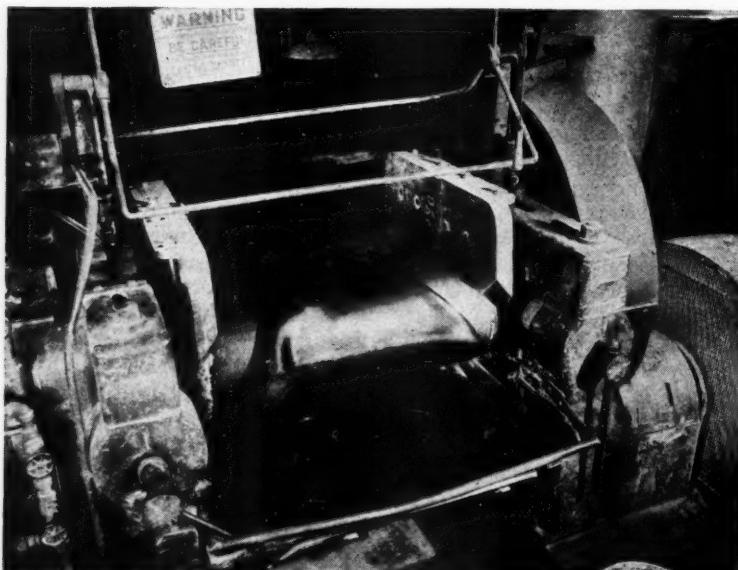


FIGURE 1. MILLING OF KOROSEAL

hard rubber to those of a jelled rubber cement embodying modified, substantially insoluble polymers of vinyl halides. By adaptations of composition and of methods of processing, a variety of useful rubber-like materials has been produced, the physical and chemical properties of which may be varied over a wide range by compounding, particularly by the choice of plasticizer. It is necessary to distinguish between plasticizers and solvents, and we shall arbitrarily term as plasticizers the relatively non-volatile materials, and as solvents, the readily volatile materials. Those soluble or insoluble materials which are not plasticizers or solvents, but which are added to modify the processing or to change the appearance or properties of the finished product will, according to

the usage common in the rubber industry, be termed "pigments." To avoid confusion, all data given in the subsequent portion of this paper will be based on vinyl chloride compounds containing a single representative plasticizer—namely, tricresyl phosphate.

Processing

Since Koroseal is thermoplastic, it can be worked under similar conditions and with the same equipment used for processing rubber. Koroseal in most of its forms may be plasticized on hot mill rolls (Figure 1), calendered to various gages, and extruded through dies to give products similar to those shown in Figure 2. Mill roll temperatures approximate 105° C. (221° F.). Because of its lack of tack, Koroseal is somewhat harder to work than most rubber compounds, but with proper care and experience no difficulty is encountered.



FIGURE 2. SHEETED, TUBED, AND CALENDERED KOROSEAL

Its softer modifications may be mixed readily in a glass-lined, steam-jacketed mixer.

Koroseal resembles rubber with respect to the trapping of air blisters, in that thin sheets (0.125 to 0.6 mm.) are usually air-free, especially if run on an odd-speed calender, while the thicker gages (0.8 mm. and above) usually have air blisters if run in a single ply. The softer stocks may be plied up at the calender into a fairly coherent sheet, although the ply adhesion is not as good as with masticated rubber.

Koroseal may be uniformly extruded in all sizes and shapes within the limits of the extruding machine. This property is very useful in the preparation of tubing for use as such or for blank stock for further processing.

In some of its forms, such as die-run tubing and the harder sheeted stocks, Koroseal may be used directly without molding, but it is more often necessary that it be molded. For this purpose, hydraulic presses with steam-heated platens are employed with either flash or plunger-type molds, dependent to some extent on the shape of the article to be prepared. Figure

3 shows a number of shapes into which the material has been formed. The softer stocks may be plied up, taped, and integrally bonded in open steam. The harder stocks should be press-molded because higher pressures are necessary for cohesion of the laminations. To prevent distortion, it is generally necessary to cool the articles in the press before removal from the mold. The average molding temperatures vary from 147° C. (297° F.) to 160° C. (320° F.), depending on the stock and size of article to be molded.

Scrap Koroseal, such as mold flash and trimmings, is easily reworked. Repeated milling and molding does not present practical difficulties and apparently produces no deterioration of the material. This property permits the reduction of losses on molded articles and does not, as in the case of rubber, necessitate a chemical treatment for reclamation. Figure 4,

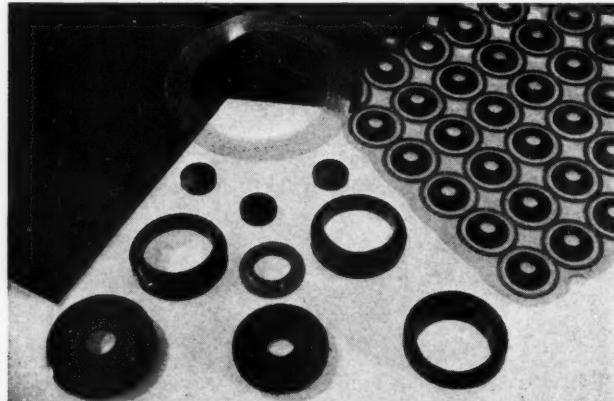


FIGURE 3. KOROSEAL MOLDED ARTICLES

where tensile strength has been plotted against time (at 147° C.) and temperature (20 minutes) of molding, respectively, shows that Koroseal is substantially unaffected by long heating at practical molding temperatures.

Koroseal in its un compounded form is a translucent material whose natural color varies, with the choice of plasticizer and with the extent of milling or molding, from a very pale amber to a dark brown.

Koroseal behaves like rubber in that it forms highly viscous solutions with solvents but is unlike rubber in that milling of the stock does not reduce the solution viscosity. The solids content of the solutions normally used is approximately 10 per cent by weight. Since gelation occurs on cooling, these solutions must be used at or near the boiling point of the solvent. However, even with these limitations, Koroseal solutions offer commercial possibilities in fields such as impregnation and coating of fabrics, coating of metal parts

such as plating racks, and coating of paper. Figure 5 shows the excellent impregnation of tire cord that is obtainable with a Koroseal solution as compared with rubber latex of the same concentration.

Compounding

Practically all of the recognized rubber-compounding materials have been incorporated with Koroseal. Each might be discussed separately, but to do so would be needless repetition. Generally speaking, these materials belong in two groups—those which are soluble in or are wet by the Koroseal, and those which are neither soluble in nor wet by the Koroseal. Included in the former group are such pigments as whiting, asbestos, clay, zinc oxide, lithopone, gas black, iron oxide, magnesia, lead oxide, and organic and inorganic colors. In the noncompatible group are such materials as factice, synthetic and natural rubbers, and nitrocellulose. The

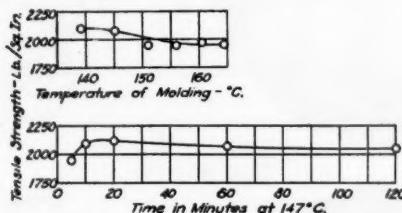


FIGURE 4. EFFECT OF TIME AND TEMPERATURE OF MOLDING ON TENSILE STRENGTH OF KOROSEAL

compatible materials when added in quantities up to 25 per cent by volume of the batch act as stiffening and coloring agents. The chief advantages to be gained by compounding Koroseal are to increase hardness, decrease resilience, and in other ways modify properties to meet service requirements. Physical tests have revealed no increase in tensile strength due to pigmentation.

Sulfur, either alone or in the presence of the common rubber accelerators or activators, gives no effects other than those shown by pigments, but when sodium sulfide is used in conjunction with the sulfur a reaction occurs on the application of heat which in effect substantially reduces the thermoplasticity of the stock. It is immediately obvious that a compound so prepared will have enhanced value in services at elevated temperatures. It is also apparent that processing is facilitated, since it is not necessary to cool the stock in the molds before removal.

Physical and Chemical Properties

The tensile strength of Koroseal compounds may be varied within wide limits. Figure 6 shows that the tensile strength

is dependent upon the proportion of plasticizer present and decreases as the latter is increased. A study of the curve will show an apparent discrepancy, in that the tensile strength increases to a maximum and then falls off. This is readily explained by the fact that compounds containing less than 15 per cent plasticizer are so hard to work that it is practically impossible to obtain a homogeneous test piece.

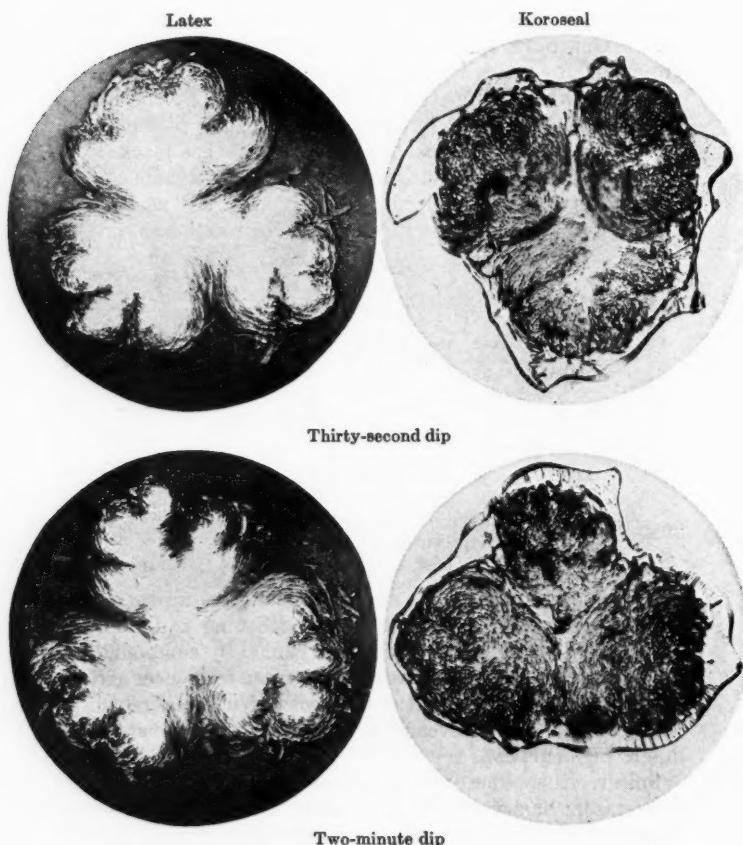


FIGURE 5. PHOTOMICROGRAPHS SHOWING IMPREGNATION OF CORD BY KOROSEAL SOLUTION AND RUBBER LATEX

As might be anticipated, the hardness decreases as the proportion of plasticizer is increased. It is interesting to note that, measured at room temperature with a Shore soft rubber durometer, the decrease in hardness is not apparent until more than 30 per cent plasticizer has been added. However, when measured at an elevated temperature, the hardness decreases uniformly with increased percentages of plasticizer.

Elongation is an inverse function of tensile strength. This condition might also be expected from the nature of the material.

Shown in Figure 7 are the stress-strain characteristics of Koroseal, synthetic rubber, and natural rubber compounds. In order for the comparison to be fair, it was made on com-

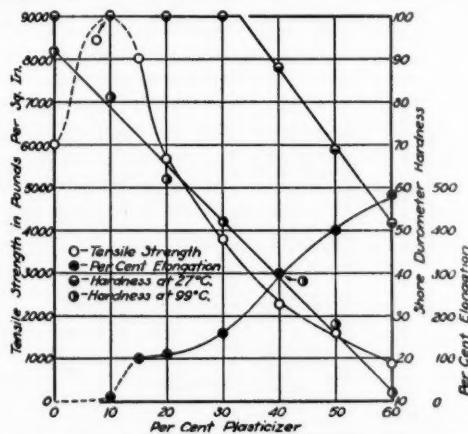


FIGURE 6. EFFECT OF PROPORTION OF PLASTICIZER ON TENSILE STRENGTH, ELONGATION, AND HARDNESS OF KOROSEAL

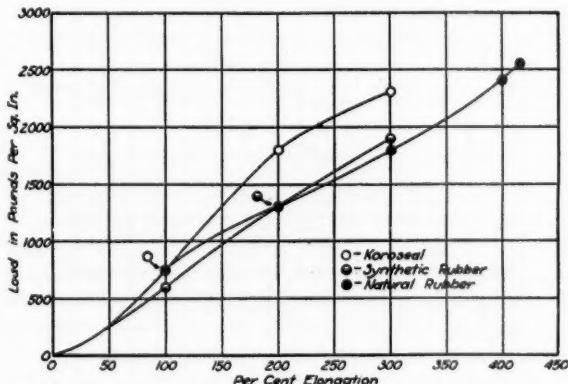


FIGURE 7. COMPARISON OF STRESS-STRAIN CHARACTERISTICS OF KOROSEAL AND OF SYNTHETIC AND NATURAL RUBBER COMPOUNDS DESIGNED FOR SERVICE IN OIL

pounds designed for and actually being used in contact with oils.

The relation of permanent set to proportion of plasticizer in the compound is illustrated in Figure 8. This characteristic was measured by cutting one-inch-square samples from $\frac{3}{32}$ -inch sheets, placing these between smooth, flat, steel plates and loading them under spring pressure to 400 pounds per

square inch. The samples were then placed in an oven at 70° C. (158° F.) for 22 hours. Ten minutes after removal from the oven the decrease in thickness was measured on a Randall-Stickney gage. The permanent set is expressed as percentage decrease of original thickness. The tests were repeated at room temperature (average 25° C.). It should be pointed out that these tests were more severe than are ordinarily encountered in most types of gasket service, and that at lower

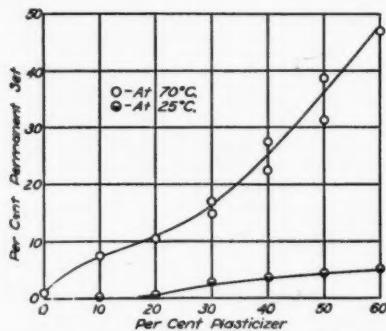


FIGURE 8. PERMANENT SET OF UNPIGMENTED KOROSEAL

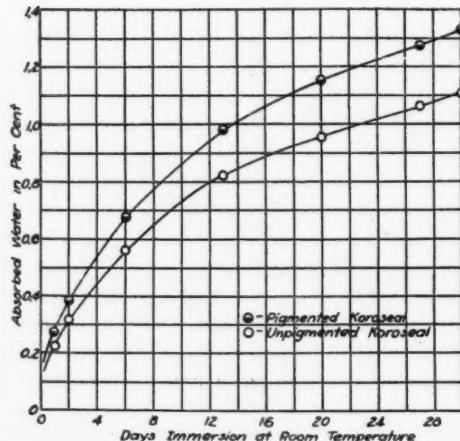


FIGURE 9. WATER ABSORPTION OF KOROSEAL

temperatures and pressures the set is practically nil. A low-set rubber motor support stock adapted for compressive service when tested as above showed 4.17 per cent set at the elevated temperature and 1.04 per cent set at room temperature.

The impact strength at room temperature of the harder compounds approximates 100 inch-pounds per square inch of cross-sectional area. Obviously the softer compounds are not

shattered on impact. Hard rubber stock used next to the metal rim of solid tires averages 35 inch-pounds per square inch.

Koroseal, like most materials containing a high percentage of halogen, will burn only when held in direct contact with a flame.

The dielectric strength or breakdown voltage varies from that of the plasticizer to above 1000 volts per mil with decreasing plasticizer content (determined at 60 cycles on sheets of 0.050 inch thickness).

Low water absorption by Koroseal is indicated by Figure 9. Results of immersion of two compounds are shown. The lower curve represents an unpigmented stock having a durometer hardness of 75, while the upper curve represents the same stock to which has been added 25 per cent by weight of African blue asbestos. Although the curves have not be-

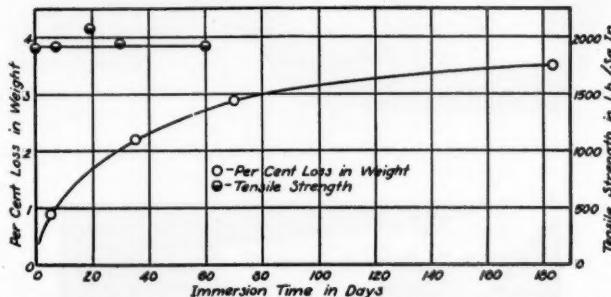


FIGURE 10. EFFECT ON KOROSEAL OF IMMERSION IN MINERAL OIL

come asymptotic in the immersion time indicated, experience has shown that water is not continually absorbed.

In flexing tests duplicating the actual service for which Koroseal and rubber units were designed, the rubber unit failed after 300,000 flexures, whereas the Koroseal compound was taken out of test while still serviceable after 3,000,000 flexures.

Uses

Resistance to moisture and stability over a wide range of operating temperatures make the extremely soft varieties of Koroseal ideal for matrix material for molding plaster of Paris and cement ornaments. Glue compositions used for this purpose frequently must be adjusted to the weather, while a single Koroseal compound will retain its desired properties throughout seasonal changes. Furthermore, recent researches on plaster of Paris have made new and better products available to the plaster-casting industry, but these new products cannot be used successfully in glue composition molds because the relatively high heat of hydration ac-

celerates the already rapid loss of mold detail. Koroseal overcomes these difficulties, as evidenced by regular factory operations in which over five hundred casts have been made in a single mold, whereas glue molds formerly used were discarded after less than one-tenth as many castings. Figure 11 shows a sample of Koroseal casting jelly, together with casts which have been taken from molds. Figure 12 shows a mold which has been used in production. This photograph illustrates to a certain extent the mold detail obtainable. There is no loss due to obsolete or misused

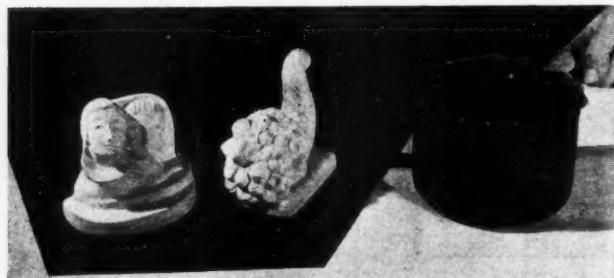


FIGURE 11. PLASTER CASTS AND KOROSEAL MOLDING JELLY



FIGURE 12. FINE DETAIL FROM KOROSEAL MOLD

molds, since the material may be recast a great number of times without impairing its properties.

The resistance to swelling and disintegration of Koroseal by vegetable and mineral oils is remarkable. In Figure 10 the changes in weight and tensile strength have been plotted against time of immersion at room temperature. In these tests a light paraffin-base oil (viscosity, 100 Saybolt seconds at 100° F.) and a heavy mineral oil (viscosity, 160 to 200 Saybolt seconds at 210° F.) were used. The effects of the two

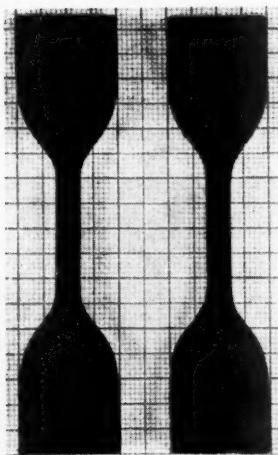
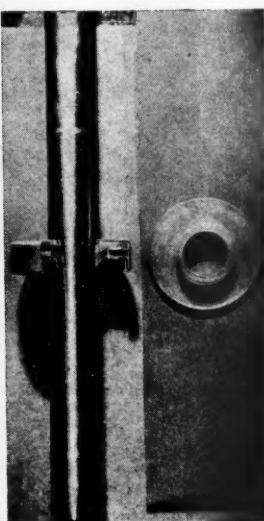


FIGURE 13. KOROSEAL DUMB-BELL TEST STRIPS BEFORE AND AFTER IMMERSION IN OIL

Left: Original
Right: After 60 days in oil at room temperature



FIGURE 14. KOROSEAL SEALING MEMBER ON RE-CIPROCATING PISTON



Courtesy, Spicer Manufacturing Company

oils are so nearly the same that the two curves are superimposed. Therefore, only the light oil has been recorded on the graph. Unlike other rubber-like materials, Koroseal shows a loss of weight and, instead of swelling, a slight shrinkage in volume when in contact with oils. This characteristic becomes progressively more apparent as the temperature is

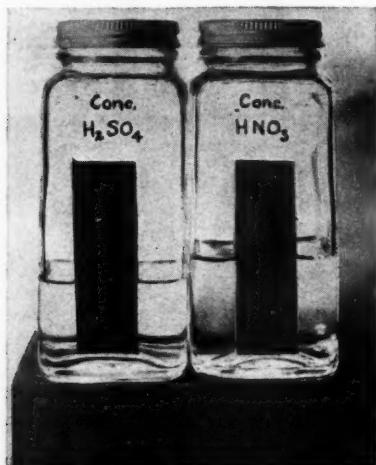


FIGURE 15. KOROSEAL AND ACID
AFTER 30-DAY IMMERSION

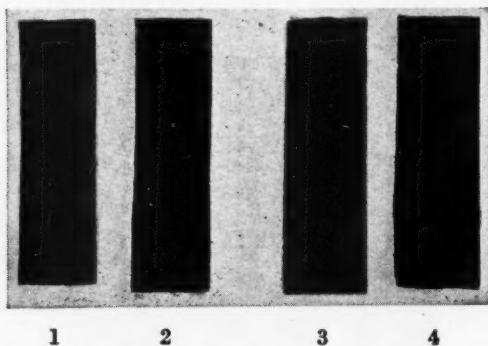


FIGURE 16. KOROSEAL STOCKS AFTER IMMERSION
IN CORROSIVE CHEMICALS FOR 30 DAYS

1. Concentrated sulfuric acid at room temperature.
2. Concentrated nitric acid at room temperature.
3. 46 per cent sodium hydroxide at room temperature.
4. 46 per cent sodium hydroxide at 70° C.

raised. However, in service tests where the temperature has risen to approximately 75° C. (167° F.), the material has maintained original properties to a surprising degree.

Figure 13 shows two test sections; one is original and the other has been immersed in the light oil, mentioned in the

foregoing, for 60 days. Comparison of the two samples will give some idea of the volume change. It has been shown previously (Figure 10) that the tensile strength is substantially unaffected in the same test.

As a gasket or a sealing member working in oil, Koroseal has been adapted to many uses. Notable among these are drip-proof service in flanged oil piping operating at 150 pounds per square inch pressure where some fifteen or twenty other materials, including paper, asbestos, rubber compositions, synthetic rubber-like products, and duck-inserted rubber, had failed; sealing members on reciprocating pistons (Figure 14) where after 17,000,000 4-inch strokes no leakage could be detected; and transformer gaskets where service conditions are quite severe.

FIGURE 17. KOROSEAL CONTAINER AFTER HOLDING CHROMIUM-PLATING SOLUTION AT 75°C. FOR 11 MONTHS



FIGURE 18- DISTORTION TO SHOW FLEXIBILITY OF KOROSEAL CONTAINER



From the inertness of the base material, one might readily anticipate the resistance of Koroseal to corrosive chemicals. Figure 15 shows test strips immersed in concentrated nitric and sulfuric acids after 30 days at room temperature. It is apparent that there is no discoloration of either acid. Figure 16 shows the strips of Figure 15 after removal from the acids, together with two strips which had been in 46 per cent sodium hydroxide. Although at elevated temperatures the alkali discolored the surface of the specimen, the physical properties were in no way impaired, and there was no discoloration of the solution. Figure 17 pictures a container which had held chromium-plating solution at 75° C. (167° F.) for 11 months. The inner surface was somewhat roughened by deposited salts, but the container was still flexible, as is shown in Figure 18.

Koroseal tubing has been used in the laboratory for transferring chlorine gas, ozone, and sulfur chloride, and shows no apparent deterioration in such service. Ball valves of Koroseal have been used for sealing outlets in chlorine-water tanks.

Koroseal compounds are extremely resistant to aging and light-cracking, both natural and accelerated. Samples which have been continuously exposed to Akron weather for over two years are still quite flexible and show no surface checking or cracking. Figure 19 illustrates the remarkable superiority of the new product over cured rubber in this test. Exposure to ultraviolet light from a mercury vapor lamp for 144 hours showed no effects; 96 hours in the Bierer bomb also was without effect.

Koroseal is not recommended where service conditions require complete immersion in organic compounds containing nitro or chlorine groups, aliphatic and aromatic ketones or

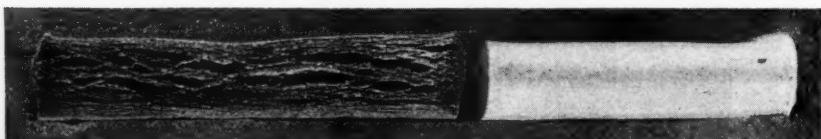


FIGURE 19. SAMPLES OF RUBBER (LEFT) AND KOROSEAL AFTER 2-YEAR ROOF AGING

esters, aromatic amino compounds, and the lower aliphatic acids. Exclusive of these, the material is resistant to all the well-known commercial heavy chemicals.

A great many other applications of Koroseal suggested by its unique combination of properties have been rather fully investigated and give promise of extensive commercial utilization.

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INDEX

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME VIII, 1935

AUTHORS

	Page
AKOBZHANOV, I. G. Synthetic Rubber. Its Industrial Production in the U. S. S. R.	430
BARNETT, C. E., AND MATHEWS, W. C. Thermal Properties of Rubber Compounds. II. Heat Generation of Pigmented Rubber Compounds.....	138
BARRON, H. Adsorptive Properties of Carbon Black. A New Angle.....	91
BARRON, HARRY. The Tensile Properties of Latex Products.....	268
BEHRE, J. The Mastication of Rubber.....	388
BEHRE, J. The Measurement of the Plasticity of Rubber.....	266
BEKKEDAHL, NORMAN. See McPherson, Archibald T.	
BEKKEDAHL, NORMAN. Forms of Rubber as Indicated by Temperature-Volume Relationship.....	5
BLAKE, JOHN T. Studies in the Vulcanization of Rubber. VI. Thermochemistry.....	112
BLOOMFIELD, G. F., AND FARMER, E. H. Research on Modified Rubbers. VI. The Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts.....	335
BLOOMFIELD, G. F., FARMER, E. H., AND MILLER, C. H. Research on Modified Rubbers. VII. Appendix. Composition of Some Chlorinated Rubbers.....	622
BLOW, C. M., AND GARNER, T. L. Fatty Acid Softeners in Rubber Compounding.....	571
BOLOTNIKOV, V., AND GUROVA, V. Determination of Free Sulfur in Rubber. I. Iodometric Method of Determination of Free Sulfur.....	87
BONDY, H. F. The Influence of Certain Colored Substances on the Autoxidation of Balata and of Rubber.....	239
BROUS, S. L., AND SEMON, W. L. Koroseal, a New Plastic. Some Properties and Uses.....	641
BRUNI, G., AND NATTA, G. The Structure of Unstretched Rubber Based on Studies with Electron Rays.....	1
BUIZOV, B. V., MOLODENSKIY, V. S., AND MIKHAILOV, N. I. The Chlorination of Disaggregated Rubber.....	371
BUIZOV, B. V., AND POPOVA, M. K. Influence of the Gaseous Medium on Hot Vulcanization.....	437
BUSSE, W. F. Tear Resistance and Structure of Rubber.....	122
CAWLEY, C. M., AND KING, J. G. The Hydrogenation-Cracking of Rubber.....	360
CUMMINGS, A. D. See Jessup, R. S.	
CUMMINGS, A. D. See McPherson, Archibald T.	
DAVEY, W. S. See Martin, G.	
DAVIES, B. L. Accelerators in Hard Rubber.....	75
DERIEUX, J. B. The Coefficient of Friction of Rubber.....	441
DILLON, J. H., AND JOHNSTON, N. Remarks on the Measurement of the Plasticity of Rubber.....	55
DOGADKIN, B., AND MARGOLINA, J. The Effect of Surface-Active Substances and Electrolytes upon the Crystallization of Sulfur from Rubber Solutions.....	250, 499
DONALD, M. B. See Stevens, H. P.	
ECCLES, J. C., AND THOMPSON, J. H. C. An Investigation of the Visco-elastic Properties of Rubber.....	177
ENDO, HIDEMARO. Studies on the Acetone Extraction of Raw Rubber. I. The Effect of the Time of Heating of the Alcohol Solution on the Determination of the Acid Value of Raw Rubber and Its Acetone Extract. II. The Influence of Heating at 100° C. and of Storing the Acetone Extract on Its Acid Value. III. Effect of the Time of Acetone Extraction of Raw Rubber on the Acid Value of the Acetone Extract and of the Acetone-Extracted Residue. IV. The Relation between the Time of Saponification and the Saponification Value of Raw Rubber and Its Acetone Extract.....	604
	605
	607
	610
FARMER, E. H. See Bloomfield, G. F.	
FERRI, CESARE. See Meyer, Kurt H.	
FRUMKIN, L., AND MARGARITOV, V. The Shock-Absorbing Quality of Rubber.....	528
FUJITA, HIRONOSUKE. See Tanaka, Yoshio.	
GARNER, T. L. See Blow, C. M.	
GERMAN, S. D. The Raman Spectrum of Rubber.....	521
GIBBONS, P. A. Semi-Ebonite. I.....	554
GRIFFITH, T. R. A Mathematical Treatment of a Theory of Rubber Structure.....	23
GUROVA, V. See Bolotnikov, V.	
HEATON, NOEL. See Stevens, H. P.	
HERRMANN, D. B. Diffusion of Water through Organic Insulating Materials.....	297
HOLT, WILLIAM L. See Smith, W. Harold.	
HOLT, WILLIAM L., AND MCPHERSON, ARCHIBALD T. A Water Bath Having Submerged Individual Sample-Containers for the Accelerated Aging of Rubber in Air.....	302
HORIE, HUKIO, AND MORIKAWA, KIKUO. Heat Changes in the Vulcanization of Rubber. I. Qualitative Tests on a Comparative Basis.....	514
JESSUP, R. S., AND CUMMINGS, A. D. Heats of Combustion of Rubber and of Rubber-Sulfur Compounds.....	44
JOHNSTON, N. See Dillon, J. H.	
JONES, F. A. See Twiss, D. F.	

	Page
KAGAN, B., AND SUKHAREVA, N. The Oxidation of Rubber by Hydrogen Peroxide.....	352
KAMBARA, SHÙ. <i>See</i> TANAKA, Y.	
KHVOLOTOVSKAYA, S., AND MARGARITOV, B. Elastic Hysteresis and Increase in Tensile Strength at Low Temperatures.....	522
KING, J. F. <i>See</i> Cawley, G. M.	
KIRCHHOF, F. The Problem of the Evaluation of Reclaimed Rubber by Analytical Methods.....	597
KUSOV, A. The Determination of the Optimum Vulcanization by Means of the Residual Elongation.....	548
LEENDERSTE, J. J. <i>See</i> Waterman, H. I.	
MACK, EDWARD, JR. The Structure of Rubber and the Mechanism of Elastic Stretching.....	192
MCGAVACK, J. Properties of Latex-Insulated Wire.....	635
McPHERSON, ARCHIBALD T. <i>See</i> Holt, William L.	
McPHERSON, ARCHIBALD T. <i>See</i> Thibodeau, Wilfred E.	
McPHERSON, ARCHIBALD T., AND BEKKEDAH, NORMAN. Heats of Reaction of the System Rubber-Sulfur.....	456
McPHERSON, ARCHIBALD T., AND CUMMINGS, ARTHUR D. Refractive Index of Rubber.....	421
MADGE, E. W. The Physico-Chemical Properties of Latex and Their Significance in Manufacture	501
MARGARITOV, V. <i>See</i> Frumkin, L.	
MARGARITOV, V. <i>See</i> Khvostovskaya, S.	
MARGOLINA, J. <i>See</i> Dogadkin, B.	
MARTIN, G., AND DAVEY, W. S. Rubber from Latex Coagulated with Sulfuric Acid.....	274
MATHEWS, W. C. <i>See</i> Barnett, C. E.	
MAX, C. G. H. <i>See</i> Waterman, H. I.	
MEYER, KURT H., AND FERRI, CESARE. The Elasticity of Rubber.....	319
MIKHAÍLOV, N. I. <i>See</i> Buisov, B.	
MILLER, C. H. <i>See</i> Bloomfield, G. F.	
MOLODENSKI, V. S. <i>See</i> Buisov, B.	
MORIKAWA, KIKUO. <i>See</i> Horie, H.	
MORRIS, V. N. <i>See</i> Park, C. R.	
NATTA, G. <i>See</i> Bruni, G.	
PARK, C. R., AND MORRIS, V. N. Dispersion of Channel Gas Black in Rubber. Effect of Stearic Acid and Other So-Called Dispersing Agents.....	470
POPOVA, M. K. <i>See</i> Buisov, B.	
PUMMERER, R. New Results on the Ozone Decomposition of Natural Rubber and of Sodium Butadiene Rubber.....	39
REDFARN, C. A. <i>See</i> Schidrowitz, P.	
REINER, MARKUS. Viscometric Studies of Rubber Solutions.....	259
RHODES, EDGAR. The Specific Gravity of Preserved Latex.....	284, 448
VAN ROSSEM, A. Plastic and Elastic Phenomena in Rubber.....	395
SACKETT, G. A. Manganese Salts in Plantation Rubber.....	305
SAYLOR, CHARLES PROFFER. <i>See</i> Smith, W. Harold.	
SCHIDROWITZ, P. Research on Modified Rubbers. V. Technological Properties of Chlorinated Rubbers from Latex.....	613
Va. Technological Properties of Rubber Oxidation Products.....	614
SCHIDROWITZ, P., AND REDFARN, C. A. Research on Modified Rubbers. VII. Expanded Chlorinated Rubber.....	616
SCHOENFELD, FRANK K. Surface Chemistry of Carbon Black. Effect on Vulcanization of Rubber	483
SCHWARZKOPF, OTTO. The Influence of Catalysts in the Reaction of Sulfur on Unsaturated Organic Substances. I. A Study of Vulcanization at Elevated Temperature.....	225
SCOTT, ARNOLD H. Specific Volume, Compressibility, and Volume Thermal Expansivity of Rubber-Sulfur Compounds.....	401
SCOTT, J. R. Theory and Application of the Parallel-Plate Plastimeter. Part 2.....	587
SEMON, W. L. <i>See</i> Brous, S. L.	
SHIMADA, KEIICHI. Studies on the Nature of the Action of Organic Accelerators for Rubber Vulcanization. VII. The Effect of Heat on the Surface Tension of Rubber Solutions.....	69
X. The Action of Organic Acids on Rubber Solns.....	73
Investigations of Unknown Components of Crude Rubber. I. Copper Content of Different Types of Crude Rubber.....	86
SMITH, W. HAROLD, AND HOLT, WILLIAM L. Vulcanization and Stress-Strain Behavior of Sol, Gel, and Total Rubber Hydrocarbon.....	210
SMITH, W. HAROLD, AND SAYLOR, CHARLES PROFFER. Ether-Insoluble or Gel Rubber Hydrocarbon. Its Solution, Crystallization, and Properties. I. Preparation and Crystallization of Gel Rubber Hydrocarbon.....	214
SNYDER, J. W. <i>See</i> Wiegand, W. B.	
STAUDINGER, H. The Constitution of Rubber and the Nature of Its Viscous Solutions.....	375
STEVENS, W. H. <i>See</i> Stevens, H. P.	
STEVENS, H. P. Rubbone.....	624
STEVENS, H. P., STEVENS, W. H., AND DONALD, M. B. Rubber in Lubricants.....	629
STEVENS, H. P., STEVENS, W. H., AND HEATON, NOEL. Rubber in Paints.....	629
SUKHAREVA, N. <i>See</i> Kagan, B.	
TANAKA, YOSHIO, KAMBARA, SHÙ, AND FUJITA, HIRONSUKE. Studies on the Joule Effect in Rubber. I. The Thermal Effect on Stretched Vulcanized Rubber.....	174
THIBODEAU, WILFRED E., AND MCPHERSON, ARCHIBALD T. Photo-elastic Properties of Soft, Vulcanized Rubber.....	183
THOMPSON, J. H. C. <i>See</i> Eccles, J. C.	
TURNER, H. Surface Cracking of Vulcanized Rubber.....	58

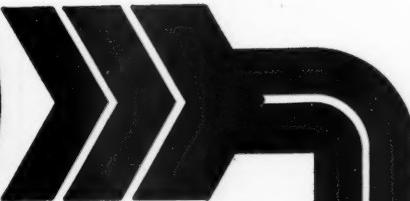
	Page
TWISS, D. F., AND JONES, F. H. The Restraining of Vulcanization in Rubber Manufacture.....	230
DE VRIES, O. The Specific Gravity of Rubber in Latex.....	443
WATERMAN, H. I., MAX, C. G. H., AND LEBENDERSTE, J. J. Preparation from Rubber of Plastic Materials Suitable for the Manufacture of Films and Threads.....	632
WINGAND, W. B., AND SNYDER, J. W. The Rubber Pendulum, the Joule Effect, and the Dynamic Stress-Strain Curve.....	151
WILLIAMS, IRA. Colloidal Changes during Rubber Vulcanization.....	102

SUBJECTS

	Page
Accelerated Aging of Rubber in Air. Water Bath Having Submerged Individual Sample Containers for the.	302
Accelerators for Rubber Vulcanization. Organic.	69
Accelerators in Hard Rubber.	75
Acetone Extraction of Raw Rubber. Part I.	604
Acetone Extraction of Raw Rubber. Part II.	605
Acetone Extraction of Raw Rubber. Part III.	607
Acetone Extraction of Raw Rubber. Part IV.	610
Acid Softeners in Rubber Compounding. Fatty.	571
Acid Value of Raw Rubber and Its Acetone Extract.	604
Acids on Rubber Solns. The Action of Organic.	73
Adsorptive Properties of Carbon Black. A New Angle.	91
Aging of Rubber in Air. Accelerated.	302
Analytical Methods. The Problem of the Evaluation of Reclaimed Rubber by.	597
Autoxidation of Balata and of Rubber.	239
 Balata. Autoxidation of.	 239
Carbon Black. Adsorptive Properties of.	91
Carbon Black. Surface Chemistry of.	483
Catalysts in the Reaction of Sulfur on Unsaturated Organic Substances. Influence of.	225
Channel Gas Black in Rubber. Dispersion of.	470
Chlorinated Rubber. Expanded.	616
Chlorinated Rubbers. Composition of Some.	622
Chlorinated Rubbers from Latex.	613
Chlorination of Disaggregated Rubber.	371
Coefficient of Friction of Rubber.	441
Colloidal Changes during Rubber Vulcanization.	102
Colored Substances on Autoxidation of Balata and of Rubber. Influence of Certain.	239
Combustion of Rubber and of Rubber-Sulfur Compounds. Heats of.	44
Composition of Some Chlorinated Rubbers.	622
Compounds. Thermal Properties of Rubber.	138
Compressibility of Rubber-Sulfur Compounds.	401
Constitution of Rubber and the Nature of Its Viscous Solutions.	375
Copper Content of Different Types of Crude Rubber.	86
Cracking of Rubber. Hydrogenation.	360
Cracking of Vulcanized Rubber. Surface.	58
Crude Rubber. Copper Content of Different Types of.	86
Crude Rubber. Unknown Components of.	86
Crystallization of Gel Rubber Hydrocarbon.	214
Crystallization of Sulfur from Rubber Solutions.	250, 499
 Determination of Free Sulfur in Rubber. I.	 87
Determination of the Optimum Vulcanization by Means of the Residual Elongation.	548
Diffusion of Water through Organic Insulating Materials.	297
Disaggregated Rubber. The Chlorination of.	371
Dispersing Agents. Effect of Stearic Acid and Other So-called.	470
Dispersion of Channel Gas Black in Rubber. Effect of Stearic Acid and Other So-called Dispersing Agents.	470
Dynamic Stress-Strain Curve.	151
Ebonite. Semi.	554
Elastic Hysteresis and Increase in Tensile Strength at Low Temperatures.	522
Elastic Phenomena in Rubber. Plastic and.	395
Elastic Properties of Rubber. Visco-	177
Elastic Stretching. The Structure of Rubber and.	192
Elasticity of Rubber.	319
Electron Rays. The Structure of Rubber Based on Studies with.	1
Electrolytes. Effect of Surface Active Substances and.	250, 499
Elongation. Determination of the Optimum Vulcanization by Means of Residual.	548
Ether-insoluble or Gel Rubber Hydrocarbon. Its Solution, Crystallization, and Properties.	214
Evaluation of Reclaimed Rubber by Analytical Methods.	597
Expanded Chlorinated Rubber.	616
Expansivity of Rubber-Sulfur Compounds.	401
Fatty Acid Softeners in Rubber Compounding.	571
Films and Threads from Rubber.	632
Forms of Rubber as Indicated by Temperature-Volume Relationship.	5
Free Sulfur in Rubber. Determination of.	87
Friction of Rubber. The Coefficient of.	441
 Gas Black in Rubber. Dispersion of Channel.	 470
Gaseous Medium on Hot Vulcanization. Influence of the.	473
Gel and Total Rubber Hydrocarbon. Vulcanization and Stress-Strain Behavior of Sol.	210
Gel Rubber Hydrocarbon. Ether-Insoluble or.	214
 Hard Rubber. Accelerators in.	 75
Heat Changes in the Vulcanization of Rubber. I. Qualitative Tests.	514
Heat Generation of Pigmented Rubber Compounds.	138
Heat on the Surface Tension of Rubber Solutions. Effect of.	69
Heats of Combustion of Rubber and of Rubber-Sulfur Compounds.	44
Heats of Reaction of the System Rubber-Sulfur.	456
Hydrogenation-Cracking of Rubber.	360
Hydrogen Peroxide. Oxidation of Rubber by.	352
Hysteresis and Increase in Tensile Strength at Low Temperatures. Elastic.	522

	Page
Index of Rubber. Refractive.	421
Insulated Wire. Properties of Latex.	635
Insulating Materials. Diffusion of Water through Organic.	297
Iodometric Method of Determination of Free Sulfur.	87
Joule Effect and the Dynamic Stress-Strain Curve. The Rubber Pendulum, the.	151
Joule Effect in Rubber. I. Thermal Effect of Stretched Vulcanized Rubber.	174
Koroseal, a New Plastic. Some Properties and Uses.	641
Latex. Chlorinated Rubbers from.	613
Latex Coagulated with Sulfuric Acid. Rubber from.	274
Latex-Insulated Wire. Properties of.	635
Latex. Physico-Chemical Properties of.	501
Latex Products. Tensile Properties of.	268
Latex. Specific Gravity of Preserved.	284, 448
Latex. Specific Gravity of Rubber in.	443
Latex. Technological Properties of.	613
Low Temperatures. Elastic Hysteresis at.	522
Lubricants. Rubber in.	629
Manganese Salts in Plantation Rubber.	305
Mathematical Treatment of a Theory of Rubber Structure.	23
Measurement of the Plasticity of Rubber.	266
Mechanism of Elastic Stretching.	192
Modified Rubbers. V. Technological Properties of Chlorinated Rubbers from Latex.	613
Modified Rubbers. Va. Technological Properties of Rubber Oxidation Products.	614
Modified Rubbers. VI. The Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts.	335
Modified Rubbers. VII. Expanded Chlorinated Rubber.	616
Modified Rubbers VII. Appendix.	622
Optimum Vulcanization by Means of the Residual Elongation.	548
Organic Accelerators for Rubber Vulcanization. VII.	69
Organic Acids on Rubber Solutions. Action of.	73
Oxidation of Rubber by Hydrogen Peroxide.	352
Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts.	335
Oxidation Products. Rubber.	614
Ozone Decomposition of Natural Rubber and of Sodium-Butadiene Rubber. New Results on the.	39
Paints. Rubber in.	627
Parallel-Plate Plastimeter. II. Theory and Application of.	587
Pendulum. The Rubber.	151
Photoelastic Properties of Soft Vulcanized Rubber.	183
Physico-Chemical Properties of Latex and Their Significance in Manufacture.	501
Pigmented Rubber Compounds.	138
Plantation Rubber. Manganese Salts in.	305
Plastic and Elastic Phenomena in Rubber.	395
Plasticity of Rubber. Measurements of.	266
Plasticity of Rubber. Remarks on the Measurement of the.	55
Plastic. Koroseal. A New.	641
Plastic Materials Suitable for Manufacture of Films and Thread. Preparation of.	632
Plastimeter. Parallel-Plate.	587
Preparation from Rubber of Plastic Materials Suitable for the Manufacture of Films and Threads.	632
Preserved Latex. Specific Gravity of.	284, 448
Properties of Latex-Insulated Wire.	635
Raman Spectrum of Rubber.	521
Raw Rubber. Acetone Extraction of.	604
Raw Rubber. Saponification of.	610
Reclaimed Rubber. The Problem of the Evaluation of.	597
Refractive Index of Rubber.	421
Remarks on the Measurement of the Plasticity of Rubber.	55
Research on Modified Rubbers. V. Technological Properties of Chlorinated Rubbers from Latex.	613
Research on Modified Rubbers. Va. Technological Properties of Rubber Oxidation Products.	614
Research on Modified Rubbers. VI. The Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts.	335
Research on Modified Rubbers. VII. Expanded Chlorinated Rubber.	616
Research on Modified Rubbers. VII. Appendix. Composition of Some Chlorinated Rubbers.	622
Residual Elongation. Determination of Optimum Vulcanisation by Means of.	548
Resistance and Structure of Rubber. Tear.	122
Restraining of Vulcanization in Rubber Manufacture.	230
Rubber from Latex Coagulated with Sulfuric Acid.	274
Rubber in Lubricants.	629
Rubber in Paints.	627
Rubbone.	624
Saponification of Raw Rubber.	610
Semi-Ebonite. I.	554
Shock-Absorbing Quality of Rubber.	528
Sodium-Butadiene Rubber. New Results on the Ozone Decomposition of Natural Rubber and of.	39
Softeners in Rubber Compounding. Fatty Acid.	571
Sol, Gel, and Total Rubber Hydrocarbons. Vulcanisation, and Stress-Strain Behavior of.	210
Sols. Action of Organic Acids on Rubber.	73
Solutions. Effect of Surface-Active Substances and Electrolytes upon Crystallisation of Sulfur from Rubber.	250, 499
Solutions. The Constitution of Rubber and the Nature of Its Viscous.	375

	Page
Solutions. The Effect of Heat on the Surface Tension of Rubber.....	69
Solutions. Viscometric Studies of Rubber.....	259
Specific Gravity of Preserved Latex.....	284, 448
Specific Gravity of Rubber in Latex.....	443
Specific Volume. Compressibility and Volume-Thermal Expansivity of Rubber-Sulfur Compounds.....	401
Spectrum of Rubber. Raman.....	521
Stearic Acid and Other So-Called Dispersing Agents.....	470
Stress-Strain Behavior of Sol, Gel, and Total Rubber Hydrocarbon.....	210
Stress-Strain Curve. The Rubber Pendulum and the.....	151
Stretched Vulcanized Rubber. The Thermal Effect on.....	174
Structure. A Mathematical Treatment of a Theory of Rubber.....	23
Structure of Rubber and the Mechanism of Elastic Stretching.....	192
Structure of Rubber. Tear Resistance and.....	122
Structure of Unstretched Rubber Based on Studies with Electron Rays. The.....	1
Studies in the Vulcanization of Rubber. VI. Thermochemistry.....	112
Studies on the Acetone Extraction of Raw Rubber.....	604
Studies on the Joule Effect in Rubber.....	174
Studies on the Nature of the Action of Organic Accelerators for Rubber Vulcanization. VII. The Effect of Heat on the Surface Tension of Rubber Solutions.....	69
Studies on the Nature of the Action of Organic Accelerators for Rubber Vulcanization. X. The Action of Organic Acids on Rubber Solns.....	73
Sulfur from Rubber Solutions.....	250, 499
Sulfur. Heats of Reaction of System Rubber.....	456
Sulfur. Influence of Catalysts in the Reaction of.....	225
Sulfur in Rubber. Determination of Free.....	87
Sulfuric Acid. Rubber from Latex Coagulated with Surface-Active Substances and Electrolytes upon the Crystallization of Sulfur from Rubber Solutions. Effect of.....	274
Surface Chemistry of Carbon Black.....	250
Surface Cracking of Vulcanized Rubber.....	483
Surface Tension of Rubber Solutions. The Effect of Heat on.....	58
Synthetic Rubber. Its Industrial Production in the U. S. S. R.....	69
Tear Resistance and Structure of Rubber.....	430
Technological Properties of Chlorinated Rubbers from Latex.....	122
Technological Properties of Rubber Oxidation Products.....	613
Temperature-Volume Relationship. Forms of Rubber as Indicated by.....	613
Tensile Properties of Latex Products.....	5
Tensile Strength at Low Temperatures. Elastic Hysteresis and Increase in.....	268
Theory and Application of the Parallel-Plate Plastimeter. Part 2.....	522
Theory of Rubber Structure. A Mathematical Treatment of a.....	587
Thermal Effect on Stretched Vulcanized Rubber.....	23
Thermal Expansivity of Rubber-Sulfur Compounds.....	174
Thermal Properties of Rubber Compounds. II. Heat Generation of Pigmented Rubber Compounds.....	401
Thermochemistry. Studies in the Vulcanization of Rubber. VI.....	138
Threads from Rubber.....	112
Total Rubber Hydrocarbon. Vulcanization, and Stress-Strain Behavior of the.....	632
U. S. S. R., Synthetic Rubber in.....	210
Visco-Elastic Properties of Rubber. An Investigation of the.....	430
Viscometric Studies of Rubber Solutions.....	177
Viscous Solutions. The Constitution of Rubber and the Nature of Its.....	259
Volume Thermal Expansivity of Rubber Sulfur Compounds. Specific Volume, and.....	375
Vulcanization, and Stress-Strain Behavior of Sol, Gel, and Total Rubber Hydrocarbon.....	401
Vulcanization at Elevated Temperature.....	210
Vulcanization. Colloidal Changes during Rubber.....	225
Vulcanization. Influence of the Gaseous Medium on.....	102
Vulcanization in Rubber Manufacture. The Restraining of.....	437
Vulcanization of Rubber. I. Heat Changes in the.....	230
Vulcanization of Rubber. Studies in the.....	514
Vulcanized Rubber. Photoelastic Properties of Soft.....	112
Vulcanized Rubber. Surface Cracking of.....	183
Vulcanized Rubber. Thermal Effect on Stretched.....	58
Water Bath Having Submerged Individual Sample Containers for the Accelerated Aging of Rubber in Air.....	174
Water through Organic Insulating Materials. Diffusion of.....	302
Wire. Properties of Latex-Insulated.....	297
	635



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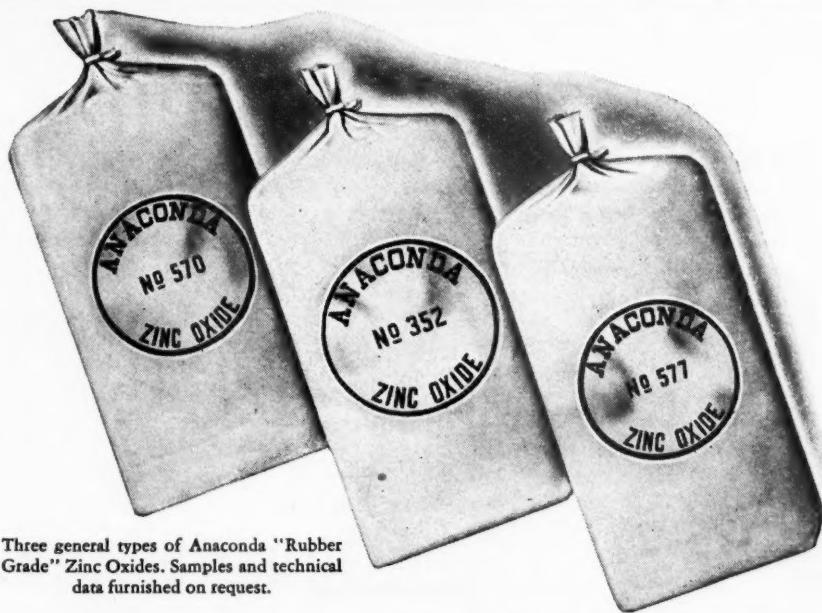
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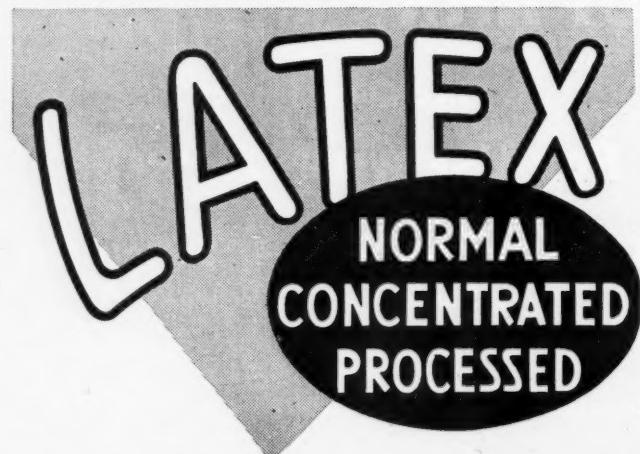
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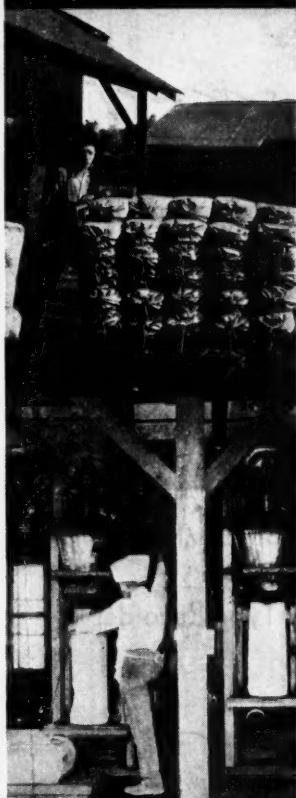
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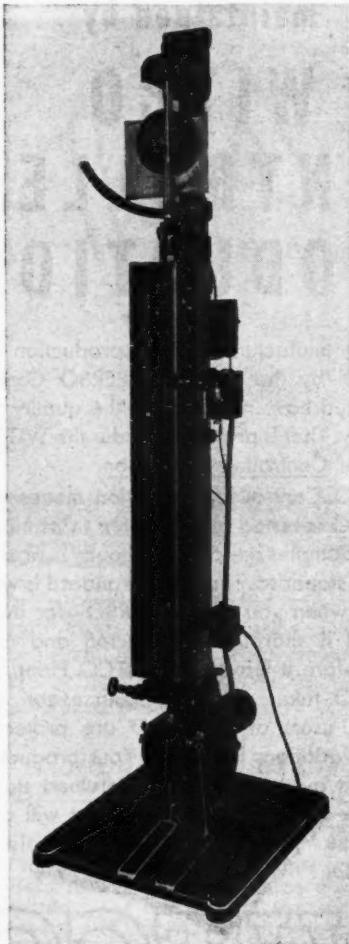


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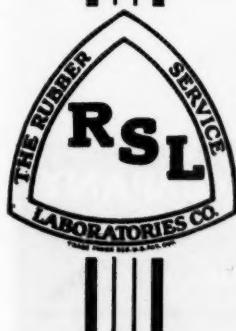
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